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401 M Street, S.W., Washington, D.C. 20460

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Sampling, workup and analysis methods were developed for six β-chloroethers in air, water soil and sediment samples to evaluate possible environmental contamination by this class of compounds. The six ethers were chloroethyl ethyl ether, chloroethyl vinyl ether, bis-(2-chloroethyl) ether, bis(2-chloroisopropyl) ether, bis(2-chloroethoxy) methane and bis(2-chloroethoxy) ethane.

Four types of samples were collected near eight industrial sites which were potential emitters of β-chloroethers. The sites included four plants where propylene oxide is produced via the chlorohydrin route. One plant produced propylene chlorohydrin; one plant produced both ethylene chlorohydrin and propylene chlorohydrin, and had produced various β-chloroethers previously; one plant produced intermediates and surfactants for the textile industry; and one plant produced polysulfide rubbers.

Air samples were collected by drawing air through Pyrex tubes packed with Tenax-GC using personnel sampling pumps. Water samples were collected either as grab samples or integrated 24-hour samples with a peristaltic pump. Soil and sediment samples were transported in glass canning jars. Air sampling tubes were desorbed with methanol with a procedure developed at MRC. Water samples were solvent extracted with methylene chloride. Soil and sediment samples were Soxhlet extracted with methylene chloride. The methylene chloride extracts from the water, soil and sediment samples were each concentrated with a Kuderna-Danish evaporator to a volume of 2-3 ml.

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bis(2-chloroethoxy) methane	sampling		
bis(2-chloroethoxy) ethane	analysis		
2-chloroethylvinyl ether	desorption		
2-chloroethylethyl ether	air		
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by

Paul L. Sherman
A. Melvin Kemmer
Leroy Metcalfe
Harlan D. Toy

Monsanto Research Corporation
Dayton, Ohio 45407

Contract 68-01-1980

Project Officer
John H. Smith

June 1978

ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF TOXIC SUBSTANCES
WASHINGTON, D.C. 20640

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Sampling, workup and analysis methods were developed for six β-chloroethers in air, water, soil and sediment samples to evaluate possible environmental contamination by this class of compounds. The six ethers were chloroethyl ethyl ether, chloroethyl vinyl ether, bis(2-chloroethyl) ether, bis(2-chloroisopropyl) ether, bis(2-chloroethoxy) methane and bis(2-chloroethoxy) ethane.

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Analysis of all of the extracts was performed by gas chromatography/mass spectrometry. The gas chromatographic column was Tenax-GC. The mass spectrometer was operated in the selected ion monitoring mode. Two characteristic ions of each compound were monitored in this mode. Detection limits for the four types of samples were: 7×10^{-7} g/m^3 for air, 2×10^{-7} g/l for water, and 4×10^{-9} g/g for soil/sediment.

Only three of the six β-chloroethers were detected in the environmental samples collected. The three ethers were bis(2-chloroethyl) ether, bis(2-chloroisopropyl) ether, and bis(2-chloroethoxy) methane. At least one of these three β-chloroethers was found in at least one sample from four of the sites. The samples from three sites in which a β-chloroether was found were all water samples. At the remaining site bis(2-chloroethoxy) methane was found in at least one sample of air, water, soil and sediment. At this same site bis(2-chloroethyl) ether was found in one water and two sediment samples.

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SECTION 1

SUMMARY

The objective of this study was to develop sampling, workup and analysis methods for the determination of trace levels of β-chloroethers in the environment near potential industrial emitters. The six β-chloroethers included in this study were: chloroethyl vinyl ether, chloroethyl ethyl ether, bis(2-chloroethyl) ether, bis(2-chloroethoxy) methane, bis(2-chloroisopropyl) ether and bis(2-chloroethoxy) ethane.

Methods were developed to sample, workup and analyze these six β-chloroethers in air, water, soil and sediment samples. The methods were validated both in the laboratory with synthetic samples and through the analysis of spiked field samples.

Air samples were collected by drawing air through Pyrex sampling tubes containing Tenax-GC with portable personnel sampling pumps. Water samples were either 24-hour integrated samples collected with a peristaltic pump or grab samples. Soil and sediment samples were collected in glass canning jars.

The Tenax-GC sampling tubes used for air samples were solvent desorbed with methanol using a procedure developed by MRC. Water, soil and sediment samples were extracted with methylene chloride. These methylene chloride extracts were concentrated with Kuderna-Danish evaporators to volumes of 2 to 3 ml.

Analysis of the extracts from the four types of samples was performed by gas chromatography/mass spectrometry. The mass spectrometer was operated in the selected ion monitoring (SIM) mode. Two characteristic ions for each compound were monitored during the SIM analysis. Average detection limits for the β-chloroethers in each type of sampling using this method of analysis were: 7×10^{-7} g/m^3 for air, 2×10^{-7} g/m^3 for water, and 4×10^{-9} g/g for soil and sediment.

Eight industrial sites were sampled during the program. During the sampling three of the six β-chloroethers were found in at least one sample. The three ethers were: bis(2-chloroethyl) ether (BCEE), bis(2-chloroisopropyl) ether (BCIPE), and bis(2-chloroethoxy) methane (BCEXM). Site one was the Olin Corporation plant at Brandenburg, Kentucky. None of the β-chloroethers were detected in the samples taken at this plant. Sampling site 2 was the Dow Chemical USA plant at Freeport, Texas. BCEE was detected in the downstream water sample closer to the plant outfall. At site 3, Jefferson Chemical at Port Neches, Texas, BCIPE was detected in the downstream water sample nearer the plant outfall. Sampling site 4 was Dow Chemical USA at Plaquemine, Louisiana. None of the β-chloroethers were detected at this site. Site 5 was the Thiokol Corporation plant at Moss Point, Mississippi. BCEXM was detected in two air, five water, one soil and two sediment samples. Also, BCEE was detected in one water and two sediment samples. Sampling at site 6, Union Carbide Corporation at Institute, West Virginia, resulted in the detection of none of the β-chloroethers. Site 7 was the Milliken Chemical plant at Inman, South Carolina. BCEE was detected in both downstream water samples. Finally, at site 8, Eastman Kodak, Rochester, New York, none of the β-chloroethers were found in the samples taken. The samples in which a β-chloroether was found are listed in Table 1. Since the sample workup did not result in 100% recovery of the β-chloroethers, a correction factor was computed for each β-chloroether in each matrix. These factors were de-

TABLE 1. SAMPLES IN WHICH β-CHLOROETHERS WERE FOUND

Sample type	Location	Company	Sample number	Sample description	β-chloroether	Concentration	ppb
Air	Moss Point, MS	Thiokol	A-7	Downwind	BCEXM	3.1×10^{-6} g/m^3	0.44
Air	Moss Point, MS	Thiokol	A-10	Downwind	BCEXM	8.4×10^{-6} g/m^3	1.2
Water	Freeport, TX	Dow	W-1	Downstream #1	BCEE	1.8×10^{-6} g/l	1.8
Water	Port Neches, TX	Jefferson	W-1	Downstream #1	BCIPE	2.2×10^{-5} g/l	22.0
Water	Moss Point, MS	Thiokol	W-1	Downstream #1	BCEXM	2.5×10^{-7} g/l	0.25
Water	Moss Point, MS	Thiokol	W-3	Outfall #1	BCEXM	1.5×10^{-4} g/l	150.
Water	Moss Point, MS	Thiokol	W-3	Outfall #1	BCEE	6.0×10^{-7} g/l	0.6
Water	Moss Point, MS	Thiokol	W-4	Downstream #2	BCEXM	5.0×10^{-7} g/l	0.5
Water	Moss Point, MS	Thiokol	W-6	Upstream	BCEXM	7.5×10^{-7} g/l	0.75
Water	Moss Point, MS	Thiokol	W-7	Outfall #2	BCEXM	1.5×10^{-4} g/l	150.
Water	Inman, SC	Milliken	W-1	Downstream #1	BCEE	4.8×10^{-6} g/l	4.8
Water	Inamn, SC	Milliken	W-2	Downstream #2	BCEE	4.6×10^{-6} g/l	4.6
Soil	Moss Point, MS	Thiokol	S-6	Downwind	BCEXM	5.8×10^{-7} g/g	580.
Sediment	Moss Point, MS	Thiokol	SD-1	Downstream #1	BCEXM	1.4×10^{-7} g/g	140.
Sediment	Moss Point, MS	Thiokol	SD-1	Downstream #1	BCEE	6.8×10^{-8} g/g	68.
Sediment	Moss Point, MS	Thiokol	SD-2	Downstream #2	BCEXM	2.3×10^{-7} g/g	23.
Sediment	Moss Point, MS	Thiokol	SD-2	Downstream #2	BCEE	1.0×10^{-8} g/g	10.

termined from results of spiked field samples for air and water samples and spiked laboratory samples in the case of soil samples. A complete discussion of the recovery studies is included in Section 7. The corrected concentrations of β-chloroethers found in the four matrices are listed in Table 1.

Additional information is listed in Tables 2 and 3 concerning other organic compounds present in representative air and water samples from some of the sampling sites. These data were acquired by making full-scan gas chromatography/mass spectrometry runs of selected samples.

In addition, three raw water samples were collected in August and September 1977 at Sioux Falls, South Dakota. These three water samples were analyzed by GC/MS/SIM for BCEE and BCIPE. Neither of these compounds was found in the three water samples. The detection limit for ethers in these samples, for which a larger volume than normal was extracted, was 3×10^{-8} g/l (0.03 ppb).

A final part of this study was devoted to: (1) synthesis of bis(1-chloromethyl-2-chloroethyl) ether, (2) identification of the compound in a simulated epichlorohydrin synthesis, and (3) GC/MS analysis of water samples from the vicinity of the Dow Chemical USA plant at Freeport, Texas, for the presence of this compound. Interest in this compound was generated by the suggestion that the compound could be a by-product of the epichlorohydrin synthesis. Five different synthesis routes were attempted unsuccessfully. Analysis of the simulated epichlorohydrin synthesis by GC/MS did reveal the presence of a compound whose mass spectra could be interpreted as being bis(1-chloromethyl-2-chloroethyl) ether. Analysis of the extracts from the water samples collected in the vicinity of the Dow plant at Freeport did not show the presence of bis(1-chloromethyl-2-chloroethyl) ether.

TABLE 2. ORGANIC CHEMICAL COMPOUNDS FOUND IN ENVIRONMENTAL SAMPLES COLLECTED IN THE β-CHLOROETHER STUDY

Compounds detected in air	Freeport, Texas	Port Neches, Tx.	Plaque-mine, La.	Moss Point Mississippi	Institute W.Va.	Inman S.C.
trichlorofluoromethane	X				X	
methylene chloride	X	X	X	X	X	
3-methyl pentane	X					
1,2-dichloroethane	X					X
trichloroethylene	X					X
toluene	X	X	X	X	X	X
chlorobenzene	X					
dibutyl phthlate	X					
benzene			X	X	X	
2,2,3,3-tetramethyl butane			X			
xylene				X		
methyl ethyl benzene				X	X	
trimethyl benzene				X		
methyl propyl benzene				X		
tetramethyl benzene				X		
acetophenone				X		X
naphthalene				X		
ethyl benzene					X	X
isopropyl benzene					X	
benzaldehyde					X	X
nitrotoluene					X	X
tetrachloroethylene						X
dichlorobenzene						X

TABLE 3. ORGANIC CHEMICAL COMPOUDS FOUND IN ENVIRONMENTAL SAMPLES COLLECTED IN THE β-CHLOROETHER STUDY

Compounds detected in water	Freeport Texas	Port Neches, Tx.	Plaque-mine, La.	Moss Point Mississippi	Insti-tute, W.Va.	Inman S.C.	Rochester N.Y.
diethyl phthalate	X	X	X		X		
di-n-butyl phthalate	X				X		
triphenyl phosphine	X		X				X
dioctyl phthalate	X	X	X		X	X	X
triphenylphosphine oxide	X	X	X	X		X	X
p-chloro phenol		X					
isothazine		X					
isobutyl phthalate		X					
2,7,11-trimethyl dodeca-2-trans-6-cis-10-trienol		X					
phenol		X					
diethylene glycol monoethyl ether		X					
α-caprolactone		X					
p-cresol		X					
triethylene glycol		X					
methyl naphthalene		X					
acenaphthalene or biphenyl		X					
nonyl phenol		X					
1,2 cyclohexane diol			X				
5-n-butyl nonane			X				
2,6-ditert-butyl-4-methyl phenol			X			X	X
stilbene			X				
2,2-dimethyl-trans-hex-3-ene			X				
diisobutyl phthalate			X				
phenyl diphenyl phosphinate			X				
1,4 oxathione				X			
methyl-ditert-butyl phenol				X			
dichlorobenzene						X	
diphenyl ether						X	
2,2,4-trimethyl pentadiol diisobutyrate						X	
butyl carbobutoxymethyl phthalate							X

SECTION 2

INTRODUCTION AND LITERATURE REVIEW

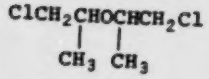
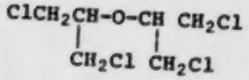
Monsanto Research Corporation (MRC) in response to Research Request No. 2 of Contract No. 68-01-1980 with the U.S. Environmental Protection Agency's office of Toxic Substances (EPA-OTS) conducted a study to measure β-chloroether levels in the environment in the vicinity of potential industrial emitters. β-Chloroethers are defined as ethers containing a chlorine atom or atoms attached to a carbon atom bonded to an ether linkage carbon atom. The original request listed the following compounds for sampling and analysis:

- bis(2-chloroethyl) ether
- bis(2-chloroisopropyl) ether
- bis(2-chloroethoxy) methane
- 2-chloroethyl vinyl ether
- 1,2-bis(2-chloroethoxy) ethane
- 2-chloroethyl methyl ether

After reviewing literature concerning the β-chloroethers, 2-chloroethyl methyl ether was removed from the list. Two compounds, 2-chloroethyl ethyl ether and bis(1-chloromethyl-2-chloroethyl) ether were added to the original list. The β-chloroethers and their abbreviations, chemical formula, structure, boiling point and density are listed in Table 4.

The remainder of this section is devoted to review of pertinent literature concerning β-chloroethers. The other sections of

TABLE 4. PROPERTIES OF β-CHLOROETHERS STUDIED

Compound	Abbreviation	Chemical formula	Structure	Boiling point, °C	Density, g/cm³
2-chloroethyl ethyl ether	CEEE	C_4H_9ClO	$ClCH_2CH_2OCH_2CH_3$	107-108	0.9894
2-chloroethyl vinyl ether	CEVE	C_4H_7ClO	$ClCH_2CH_2OCH=CH_2$	108	1.0475
bis(2-chloroethyl) ether	BCEE	$C_4H_8Cl_2O$	$ClCH_2CH_2OCH_2CH_2Cl$	178	1.2199
bis(2-chloroisopropyl) ether	BCIPE	$C_6H_{12}Cl_2O$	 $ClCH_2\underset{CH_3}{CH}O\underset{CH_3}{CH}CH_2Cl$	187	1.1034
bis(2-chloroethoxy) methane	BCEXM	$C_5H_{10}Cl_2O_2$	$ClCH_2CH_2-OCH_2OCH_2CH_2Cl$	206	1.225
1,2 bis(2-chloroethoxy) ethane	BCEXE	$C_6H_{12}Cl_2O_2$	$ClCH_2CH_2OCH_2CH_2OCH_2CH_2Cl$	230	1.197
bis(1-chloromethyl,2-cnloroethyl ether	BCMCEE	$C_6H_{10}Cl_4O$	 $ClCH_2\underset{CH_2Cl}{CH}-O-\underset{CH_2Cl}{CH}\ CH_2Cl$		

this final report, listed below, detail the information concerning the β-chloroether sampling and analysis.

- Sampling Site Selection
- Sampling Methods
- Sample Workup Methods
- Sample Analysis Methods
- Recovery Studies
- Sampling Site Descriptions and Results
- References

2.1 DESCRIPTION OF INDUSTRIAL PROCESSES INVOLVING β-CHLOROETHERS

Most data on the manufacture and uses of β-chloroethers were over ten years old and very limited. The available information pertained primarily to bis(2-chloroethyl) ether and bis(2-chloroisopropyl) ether. Information on bis(2-chloroethoxy) methane and 2-chloroethyl vinyl ether was limited. Very little information was obtained concerning 1,2-bis(2-chloroethoxy) ethane and almost none was available on 2-chloroethyl methyl ether.

2.1.1 β-Chloroether Consumption and Uses

Basically, β-chloroether usage can be divided into two main categories: (a) applications that use β-chloroethers as chemical intermediates, and (b) applications that use the physical properties of β-chloroethers as solvents (1). The consumption and use of β-chloroethers is summarized in Table 5.

Related compounds likely to be found with β-chloroethers are the α-chloroethers since chlorination first occurs by substitution of a chlorine atom on the α position of the ether (30). A closer study of the α-haloethers indicates that since α-chloroethers hydrolyze very rapidly in water (30-35), their presence in air, water, or soil for any extended period of time is very unlikely.

TABLE 5. PRODUCTS AND USES OF β-CHLOROETHERS

β-Chloroether	
Bis(2-chloroethyl) ether (1-17)	Chemical intermediate for the synthesis of morpholine, divinyl ether, plasticizers, synthetic rubber, pharmaceuticals, resins, amino ethers, β-(β-chloroethoxy) phenetole, surfactants, β-chloroethyl vinyl ether, 4,4-dicarboxyethyl,β,β'-diiododiethyl ether, tetrahydropyran 4-carbonylic acid, and 4-cyan tetrahydropyran 4-carboxylate.
	Dewaxing agent for lubricating oils.
	Solvent for the separation of butadiene from butylene.
	Penetrant, welting agent, and solvent in the textile industry.
	Insecticide, acaricide, nematocide, soil fumigant and disinfectant.
	Drycleaning agent.
	Gasoline additive to scavenge lead deposits.
	Replacement for NaOH in Kier boiling.
	Impact resistant styrene copolymer.
	Water-soluble cation-active polymeric electrolyte in papermaking industry.
	Solvent for fats, oils, waxes, resins, balsams and dyes.
	Process and pickling inhibitor.

TABLE 5 (CONTINUED). PRODUCTS AND USES OF β-CHLOROETHERS

Bis(2-chloroisopropyl) ether (1-3, 18, 19)	Chemical intermediate for dyes, resins, and pharmaceuticals.
	Soap additive in the textile industry.
	Surfactants, wetting agents, emulsifiers, and detergents.
	Wood preservative (with pentachlorophenol sodium salt).
	Solvent for fats, waxes, and greases in paints, varnish removers, spotting agents, and cleaning solutions.
Bis(2-chloroethoxy) methane (20)	Polysulfide crude rubbers for printing rollers, hose, gaskets, and gas meter diaphragms.
	Polysulfide liquid polymers for sealants and adhesives.
	Polysulfide latexes.
1,2-Bis(chloroethoxy) ethane (15, 16, 21-25)	Chemical intermediate for insecticides and other organic compounds.
	Cleaning agent.
	Polyhydroxy polysulfide polymers in paint, lacquer or varnish, plastics and resins.
	Water-soluble cation-active polymeric polyelectrolytes used in paper making industry.

TABLE 5 (CONTINUED). PRODUCTS AND USES OF β-CHLOROETHERS

	Process and pickling inhibitor in paint manufacture.
	Solvent for hydrocarbon oils, etc.; extractant.
	Water-resistant resins.
	Processing chemical in manufacture of abrasive articles from butadiene polymers and copolymers.
2-Chloroethyl vinyl ether (26-29)	Soil, oil and water resistant finishing agent for cotton, wool and polyester textiles.
	Copolymer with maleic anhydride in benzene.
	Copolymer with isobutyl vinyl ether.
	Copolymer with ethyl acrylate.
2-Chloroethyl methyl ether	No use reported in the literature.

2.1.2 β-Chloroether Production

Table 6 summarizes the chemical processes available for the synthesis of the β-chloroethers. Only bis(2-chloroethyl) ether and bis(2-chloroisopropyl) ether are produced in large enough quantities to warrant inclusion in Stanford Research Institute's Directory of Chemical Producers.

2.1.3 β-Chloroethers Formed as By-products

2.1.3.1 Bis(2-Chloroethyl) Ether--

Bis(2-chloroethyl) ether is formed as a by-product during the chlorohydrination process for the manufacture of ethylene chlorohydrin, ethylene oxide and ethylene glycol (41, 42).

Ethylene chlorohydrin--In the manufacture of ethylene chlorohydrin dilute hypochlorous acid is reacted with ethylene gas (1, 33, 42, 44).

$$CH_2{=}CH_2 + HOCl \longrightarrow CH_2ClCH_2OH \qquad (1)$$

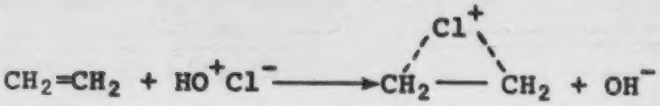
Various procedures have been developed for the production of hypochlorous acid, but it is best produced by the reaction of chlorine with water (36, 43).

$$Cl_2 + H_2O \rightleftarrows HOCl + HCl \qquad (2)$$

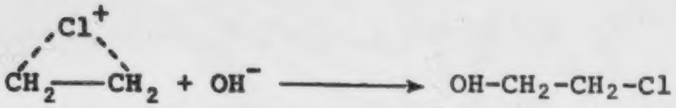
The reaction is an equilibrium and may be shifted to the product-side by using a large amount of water or by neutralizing or otherwise removing HCl from the reaction zone. Formation of bis (2-chloroethyl) ether during chlorohydrin synthesis can be represented by the equation (36, 43),

TABLE 6. MANUFACTURING PROCESS OR SYNTHESIS METHODS FOR PRODUCTION OF β-CHLOROETHERS

β-chloroether	Manufacturing process or synthesis
Bis(2-chloroethyl) ether	1. Prepared by heating ethylene chlorohydrin with sulfuric acid at 90-100°C. $2ClCH_2CH_2OH \xrightarrow{H_2SO_4} ClCH_2CH_2OCH_2CH_2Cl + H_2O$ 2. Prepared by saturating an aqueous solution of ethylene chlorohydrin with chlorine and ethylene (1, 3).
Bis(2-chloroisopropyl) ether	1. Prepared by reacting hypochlorous acid with propylene. Several reactions occur including chlorohydrination. Formation of bis(2-chloroisopropyl) ether is favored by high chlorohydrin concentration (36). 2. Prepared from β-chloroisopropyl alcohol by the H_2SO_4 process. $ClCH_2CH(CH_3)OH \xrightarrow{H_2SO_4} ClCH_2CH(CH_3)OCH(CH_3)CH_2Cl$
Bis(2-chloroethoxy) methane	Prepared by the condensation of ethylene chlorohydrin with anhydrous formaldehyde in the presence of an azeotroping agent. $2ClCH_2CH_2OH + HCHO \longrightarrow$ $ClCH_2CH_2OCH_2OCH_2CH_2Cl + H_2O$
1,2-Bis(2-chloroethoxy) ethane	Prepared in the reaction of Cl_2, ethylene and water. Up to 2% bis(2-chloroethyl) ether can be added to the reaction mixture to increase yield (37).
2-Chloroethyl vinyl ether	Prepared by the dehydrochlorination of bis(2-chloroethyl) ether. $ClCH_2CH_2OCH_2CH_2Cl \xrightarrow[NaOH]{\text{hot flake}} ClCH_2CH_2OCH = CH_2$
2-Chloroethyl methyl	1. Prepared by addition of Cl_2 and MeOH to ethylene. The yields can be greatly increased by using ethylene oxide, propylene oxide or epichlorhydrin as acid binding agents (38, 39) 2. Prepared by the action of PCl_5 on $MeOCH_2CH_2OH$ (40)



(3)



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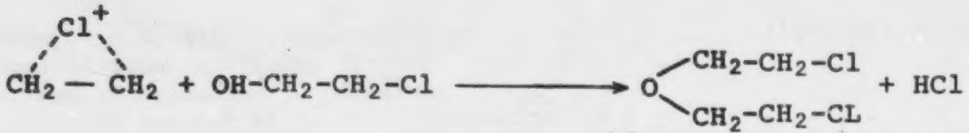


(5)

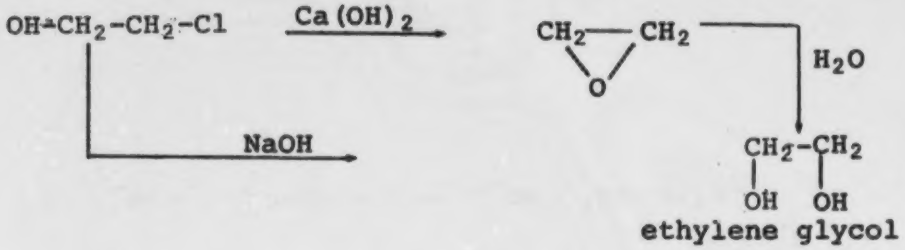
bis(2-chloroethyl) ether

The amount of bis(2-chloroethyl) ether can be controlled by the ethylene chlorohydrin concentration (36).

Ethylene oxide (by the chlorohydrin process)--The manufacture of ethylene oxide by the chlorohydrination of ethylene does not appear to have been used since 1972 (38). Currently, ethylene oxide is made by direct oxidation of ethylene over silver catalyst (1, 42). Facilities for ethylene oxide manufacture by the chlorohydrin process have been converted to make propylene oxide. Direct oxidation process being more energy intensive, energy/economic considerations could lead to a rapid return to the chlorohydrin route (1). Ethylene oxide is obtained by the hydrolysis of ethylene chlorohydrin (obtained from ethylene above) using milk of lime slurry or a solution of sodium hydroxide (1, 42).

Ethylene glycol (by the chlorohydrin process)--The manufacture of ethylene glycol via the ethylene chlorohydrin process takes in two basic steps (42):

$$CH_2{=}CH_2 + HOCl \longrightarrow OH{-}CH_2{-}CH_2{-}Cl \qquad (6)$$



(7)

Ethylene oxide can readily be converted to ethylene glycol by the action of a dilute aqueous solution of a strong acid or by reaction with water at elevated temperatures and pressures (42). A third alternative is the vapor phase hydrolysis of ethylene oxide over a silver oxide catalyst (42).

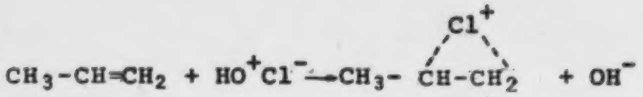
Because of the conversion to the direct oxidation process for the manufacture of ethylene oxide from the chlorohydrin process, plants using chlorohydrination have been converted to produce propylene chlorohydrin and propylene oxide. Ethylene glycol is made mainly from ethylene oxide. Only one plant is currently using the ethylene chlorohydrin process to make ethylene chlorohydrin.

2.1.3.2 Bis(2-chloroisopropyl Ether--

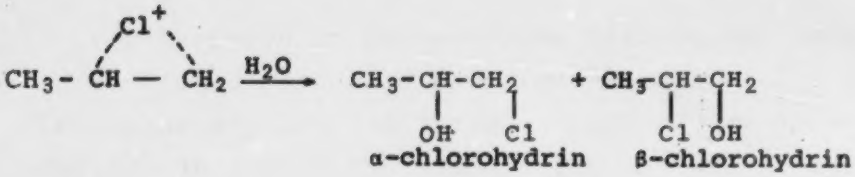
Bis(2-chloroisopropyl) ether is formed as a by-product during the chlorohydrination process for the manufacture of propylene chlorohydrin, propylene oxide and propylene glycol (36, 44).

Propylene chlorohydrin--The propylene chlorohydrin route to propylene oxide still enjoys a competitive economic position (1). Approximately 70% of the capacity is based on chlorohydrination as opposed to peroxidation (direct oxidation) (1).

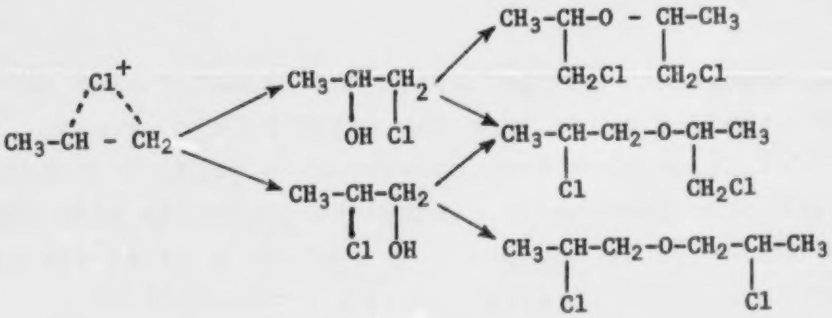
As with ethylene chlorohydrin, propylene chlorohydrin is formed by reacting hypochlorous acid with propylene. However, two chlorohydrins are possible with propylene chlorohydrin and as a result three ethers may be found. The reaction can be represented by the equation (1, 36, 44).


CH3-CH=CH2 + HO+Cl− → CH3- CH-CH2 + OH−
Cl+

(8)

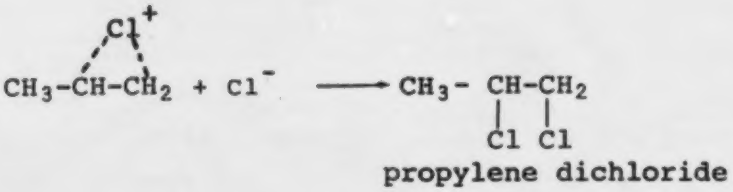

Cl+
CH3- CH — CH2
H2O
CH3-CH-CH2
OH Cl
+ CH3-CH-CH2
Cl OH
α-chlorohydrin
β-chlorohydrin

(9)


Cl+
CH3-CH - CH2
CH3-CH-CH2
OH Cl
CH3-CH-CH2
Cl OH
CH3-CH-O - CH-CH3
CH2Cl CH2Cl
CH3-CH-CH2-O-CH-CH3
Cl CH2Cl
CH3-CH-CH2-O-CH2-CH-CH3
Cl Cl

(10)

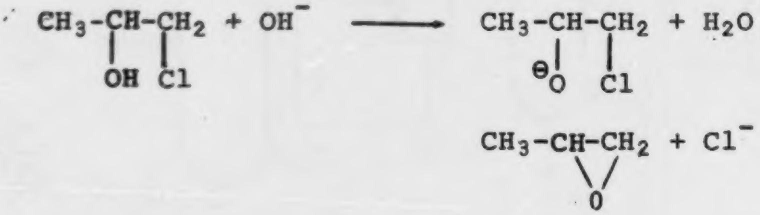
α-Chlorohydrin is the major product, because of the stability of the secondary carbon atom, but the isomer ratio has been reported to vary from 3:1 to 9:1. The major ether isomer is the bis(2-chloroisopropyl) ether (1, 36, 44). Propylene dichloride is the major by-product being produced in larger quantities with the ethers (1, 36, 44).


Cl+
CH3-CH-CH2 + Cl− → CH3- CH-CH2
Cl Cl
propylene dichloride

(11)

Propylene oxide--A typical chlorohydrin plant for manufacturing propylene oxide is shown in Figure 1. The haloether would be found at the same locations as crude propylene dichloride (e.g., in the chilled caustic soda wash of unreacted gases and in the aqueous effluent from the steam heat flash hydrolyses (1, 36, 44).

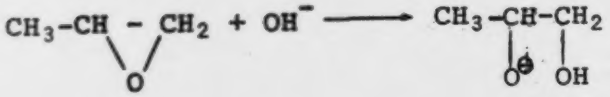
Propylene oxide is formed from propylene chlorohydrin by the action of aqueous alkali. Usually the alkali is a lime water slurry containing 10% in lime (1, 36, 44).



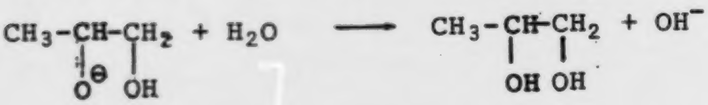
(12)

The equilibrium lies well to the right and is driven further in that direction by the removal of oxide by stripping or by reaction to glycol (1, 36, 44).

Propylene glycol--Propylene oxide can be rapidly hydrated to monopropylene glycol by the alkaline condition in the reactor (1, 36, 44).

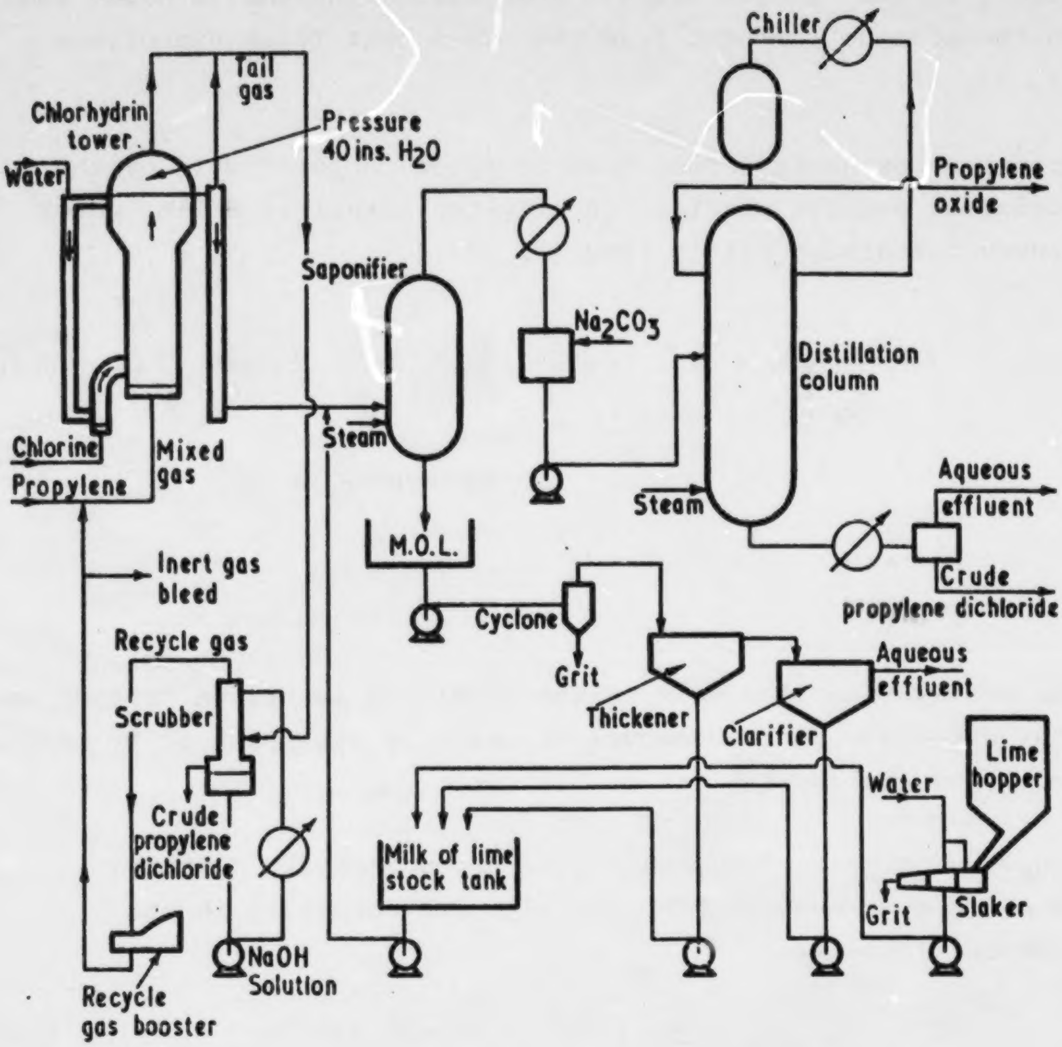


(13)



(14)

$$CH_3\text{-}\underset{O^{\ominus}}{CH}\text{-}\underset{OH}{CH_2} + H_2O \longrightarrow CH_3\text{-}\underset{OH}{CH}\text{-}\underset{OH}{CH_2} + OH^- \qquad (14)$$



Tail gas
Chlorhydrin tower.
Pressure 40 ins. H_2O
Water
Saponifier
Chiller
Propylene oxide
Na_2CO_3
Distillation column
Chlorine
Propylene
Mixed gas
Steam
Steam
Aqueous effluent
M.O.L.
Crude propylene dichloride
Inert gas bleed
Cyclone
Recycle gas
Grit
Aqueous effluent
Scrubber
Thickener
Clarifier
Lime hopper
Water
Crude propylene dichloride
Milk of lime stock tank
Grit
Slaker
NaOH Solution
Recycle gas booster

Figure 1. Diagram of a typical chlorohydrin propylene oxide plant (Fyvie [36], 1964). (reprinted with permission)

2.1.4 β-Chloroether Users

The major commercial applications of β-chloroethers can be grouped into two general areas:

- chemical intermediates, and
- solvent use.

Because of the many but limited uses of β-chloroethers, we will consider only the commercially important use of bis(2-chloroethoxy) methane in polysulfide rubbers.

2.1.4.1 Bis(2-chloroethoxy) Methane--

Bis(2-chloroethoxy) methane finds its major application as the principal monomer in polysulfide polymers (20, 1). The chemical is manufactured by Thiokol at Moss Point, Mississippi and is totally consumed in the production of polysulfides (1, 20). These specialty polymers are used as room-temperature-curing liquid polymers in the sealant and adhesive markets because of their good solvent resistance, low-temperature performance, and weathering and ozone resistance. The polymers are formed by polycondensation of the bis(2-chloroethoxy) methane with an aqueous polysulfide solution. Frequently, 1,2,3-trichloropropane is added for cross-linking and in some instances bis(4-chlorobutoxy) methane or bis(4-chlorobutyl) ether are used in minor amounts to improve low-temperature performance (1, 20).

2.1.5 Chemical Production Plant Sites With the Potential for Release of β-Chloroethers

The greatest potential for environmental emission of β-chloroethers appears to be from the inadvertent production of these chemicals in other industrial processes such as the chlorohydrin process. Other likely sources are the production and usage of β-chloroethers. Table 7 lists all potential emission sources of β-chloroethers.

TABLE 7. CHEMICAL PRODUCTION PLANT SITES WITH POTENTIAL FOR RELEASE OF β-CHLOROETHERS (45)

β-chloroether associated	Chemical produced	Company	Plant site
BCEE	Ethylene chlorohydrin	Union Carbide Corp.	Institute and South Charleston, W. Va.
BCEE	Ethylene oxide	Allied Chem. Corp. Specialty Chem. Div.	Orange, Texas (on stand-by)
		BASF Wyandotte Corp. Indust. Chems. Group	Geismar, Louisiana
		Calcasieu Chem. Corp.	Lake Charles, La.
		Celanese Corp.	
		Celanese Chem. Co., Div.	Clear Lake, Texas
		Dow Chem. U.S.A.	Freeport, Texas Plaquemine, La.
		Eastman Kodak Co. Eastman Chem. Products. Inc. subs. Texas Eastman Co., div.	Longview, Texas
		Northern Natural Gas Co.	
		Northern Petrochem. Co., subs. Polymers div.	Morris, Illinois
		Olin Corp. Design Products Div.	Brandenburg, Kentucky
		PPG Indust., Inc. Chem. Div. Houston Chem. Co. div.	Beaumont, Texas
		PPG Indust. (Caribe)	Guayanilla, P.R.
		Shell Chem. Co. Base Chems.	Geismar, Louisiana
		SunOlin Chem. Co.	Claymont, Delaware
		Texaco, Inc. Jefferson Chem. Co., Inc. subs.	Port Neches, Texas

TABLE 7. (CONT'D). CHEMICAL PRODUCTION PLANT SITES WITH POTENTIAL FOR RELEASE OF β-CHLOROETHERS (45)

β-chloroether associated	Chemical produced	Company	Plant site
BCEE	Ethylene oxide (cont'd.)	Union Carbide Corp. Chems. and Plastics Div.	Seadrift, Texas Taft, Louisiana
		Union Carbide Caribe, Inc., subs.	Penuelas, P.R.
		ADD Processing Corp.	Abbeville, Louisiana
BCEE	Ethylene glycol	Allied Chem. Corp. Specialty Chems. Div.	*Orange, Texas (on stand-by)
		BASF Wyandotte Corp. Indust. Chems. Group	Geismar, Louisiana
		Calcasieu Chem. Corp.	Lake Charles, La.
		Celanese Corp. Celanese Chem. Co., div.	Clear Lake, Texas
		Dixie Chem. Co.	Bayport, Texas
		Dow Chem. U.S.A.	Freeport, Texas Plaquemine, La.
		Eastman Kodak Co. Eastman Chem. Products, Inc., subs. Texas Eastman Co., div.	Longview, Texas
		ICI United States Inc. Specialty Chems. Div.	New Castle, Delaware
		Northern Natural Gas Co. Northern Petrochem. Co., subs. Polymers Div.	Morris, Illinois
		Olin Corp. Designed Products Div.	Brandenburg, Kentucky
		PPG Indust., Inc. Chem. Div. Houston Chem. Co., div.	Beaumont, Texas

TABLE 7 (CONT'D). CHEMICAL PRODUCTION PLANT SITES WITH POTENTIAL FOR RELEASE OF β-CHLOROETHERS (45)

β-chloroether associated	Chemical produced	Company	Plant site
	Ethylene glycol (cont'd.)	PPG Indust. (Caribe)	Guayanilla, P.R.
		Shell Chem. Co.	
		Base Chems.	Geismar, Louisiana
		Texaco, Inc.	
		Jefferson Chem. Co., Inc., subs.	Port Neches, Texas
		Union Carbide Corp. Chem. and Plastics Div.	Seadrift, Texas Taft, Louisiana
		Union Carbide (Caribe), Inc. subs.	Penuelas, P.R.
BCEE	BCEE	Buckman Labs Inc.	Cadet, Missouri Memphis, Tennessee
		J. T. Baker Chem. Co.	--
		Chemical Samples Co.	Columbus, Ohio
		Eastman Organic Chem.	Rochester, New York
		E. M. Laboratories Inc.	--
		Fisher Scientific Co.	--
		MC&B Manufacturing Chemists	--
		Union Carbide Corp.	--
BCIPE	Propylene chlorohydrin	Eastman Kodak Co.	
		Eastman Organic Chems.	Rochester, New York
		RSA Corp.	Ardsley, New York
BCIPE	Propylene oxide	BASF Wyandotte Corp.	
		Indust. Chems. Group	Wyandotte, Michigan
		Dow Chem. U.S.A.	Freeport, Texas Plaquemine, Louisiana

TABLE 7 (CONT'D). CHEMICAL PRODUCTION PLANT SITES WITH POTENTIAL FOR RELEASE OF β-CHLOROETHERS (45)

β-chloroether associated	Chemical produced	Company	Plant site
BCIPE	Propylene oxide (cont'd.)	Olin Corp. Designed Products Div.	Brandenburg, Kentucky
		Oxirane Chem. Co.	Bayport, Texas
		Texaco, Inc. Jefferson Chem. Co., Inc., subs.	Port Neches, Texas
BCIPE	Propylene glycol	Dow Chem. U.S.A.	Freeport, Texas Plaquemine, Louisiana
		Olin Corp. Designed Products Div.	Brandenburg, Kentucky
		Oxirane Chem. Co.	Bayport, Texas
		Texaco, Inc. Jefferson Chem. Co., Inc., subs.	Port Neches, Texas
		Union Carbide Corp. Chems. and Plastics Div.	Institute and South Charleston, W. Va.
BCIPE	BCIPE	Dow Chem. U.S.A.	Freeport, Texas
		Chemicals Samples Co.	Columbus, Ohio
		MC&B Manufacturing Chemicals	--
BCEM	Polysulfide polymers	Diamond Shamrock	Ashtabula, Ohio
		The Flamemaster Corp. Chem-Seal Corp. div.	Sun Valley, California
		Products Research & Chem. Corp. Eastern Sales & Mfg. Div.	Gloucester City, N. J.
		Western Mfg. Div.	Glendale, California
		Sybron Corp. Kerr Mfg. Co. Div. Acco Polymers Div.	Romulus, Michigan
		Thiokol Corp. Chem. Div.	Moss Point, Miss.

TABLE 7 (CONT'D). CHEMICAL PRODUCTION PLANT SITES WITH POTENTIAL FOR RELEASE OF β-CHLOROETHERS (45)

β-chloroether associated	Chemical produced	Company	Plant site
BCEM	Epichlorohydrin	Dow Chem. U.S.A.	Freeport, Texas
		Shell Chem. Co. Base Chem.	Deer Park, Texas Norco, Louisiana
BCEM	BCEM	Bio Chemical Labs	Smithtown, New York
		K & K Labs	--
		Mide Chem. Corp.	Bohemia, New York
BCOE	BCOE	J. T. Baker Chem. Co.	--
		Columbia Org. Chem. Co.	Columbia, S. Carolina
		Chemical Procurement Labs	College Point, N. Y.
		Chemical Samples Co.	Columbus, Ohio
		MC&B Manufacturing Chemists	--
		Polyscience, Inc.	Warrington, Pa.
		Union Carbide Corp.	--

2.2 DETECTION OF HALOETHERS IN THE ENVIRONMENT

The vast majority of reports of detection of β-chloroethers in the environment have been from water samples. However, a group of workers at Research Triangle Institute (46) have reported the detection of BCIPE in ambient air in Freeport, Texas. The levels they reported were 27 ng/m^3 and 333 ng/m^3. Since Rosen, et al (47) discovered the presence of BCEE in the Kanawha River of West Virginia in 1964, a number of other government workers have reported the detection of β-chloroethers in industrial wastewater, river water, and drinking water. Table 8 summarizes the β-chloroethers found in water, their concentration if determined, the location where they were found, and the reference where they were reported. Figure 2 is a map of the United States showing the locations where β-chloroethers have been detected.

2.2.1 Hydrolytic Stability of β-Chloroethers

A few studies have been conducted to determine the hydrolytic stability of β-chloroethers in acid, neutral, and basic aqueous systems.

Böhme and Sell (32) measured the hydrolysis rate of BCEE in a dioxane-water mixture (20M water in dioxane) at 100°C. The half life of BCEE under these conditions was 12.8 days. Van Duuren and co-workers (31) measured the kinetics of hydrolysis of microliter quantities of six chloroethers in 10 ml of a water-formaldehyde (3:1) solution. The hydrochloric acid formed was titrated with an automatic recording titrator. They found the half life of all the ethers with alpha-chloro substituents was less than 2 minutes, the half life of ethers with no alpha-chloro substitution was greater than 23 hours, and the BCEE half life was >23 hours. Salomaa and associates (33) have studied the hydrolysis of chlorovinyl ethers and chloro-substituted

TABLE 8. β-CHLOROETHERS DETECTED IN WATER

Compounds	Concentration µg/l	Location	Reference
bis(2-chloroethyl) ether	*	Kanawha River, West Virginia	47
bis(2-chloroethyl) ether	*	Jefferson Parish #2	48
bis(2-chloroisopropyl) ether	*	Jefferson Parish #2	48
bis(2-chloroethyl) ether	*	Evansville, Indiana Drinking Water	49
bis(2-chloroisopropyl) ether	0.5-5.0 2.0	Evansville, Indiana	49
bis(2-chloroethyl) ether	0.07	Carrollton	50
	0.16	Jefferson Parish #1	50
	0.12	Jefferson Parish #2	50
bis(2-chloroisopropyl) ether	0.18	Carrollton	50
	0.05	Jefferson Parish #1	50
	0.03	Jefferson Parish #2	50
bis(2-chloroethoxy) methane	140,000	Synthetic Rubber Plant	51
bis(2-chloroethyl) ether	160	Synthetic Rubber Plant	51
bis(2-chloroisopropyl) ether	*	Glycol Plant, Thickening and Sediment Pond	51
bis(2-chloroethyl) ether	10	Philadelphia Northeast, Water Treatment Plant	52
bis(2-chloroethyl) ether	0.4	Delaware River, Philadelphia	52
bis(2-chloroethyl) ether	0.01-0.36	Various Cities During NOMS	53
bis(2-chloroisopropyl) ether	0.02-0.55	Various Cities During NOMS	53

* Detected but not quantified

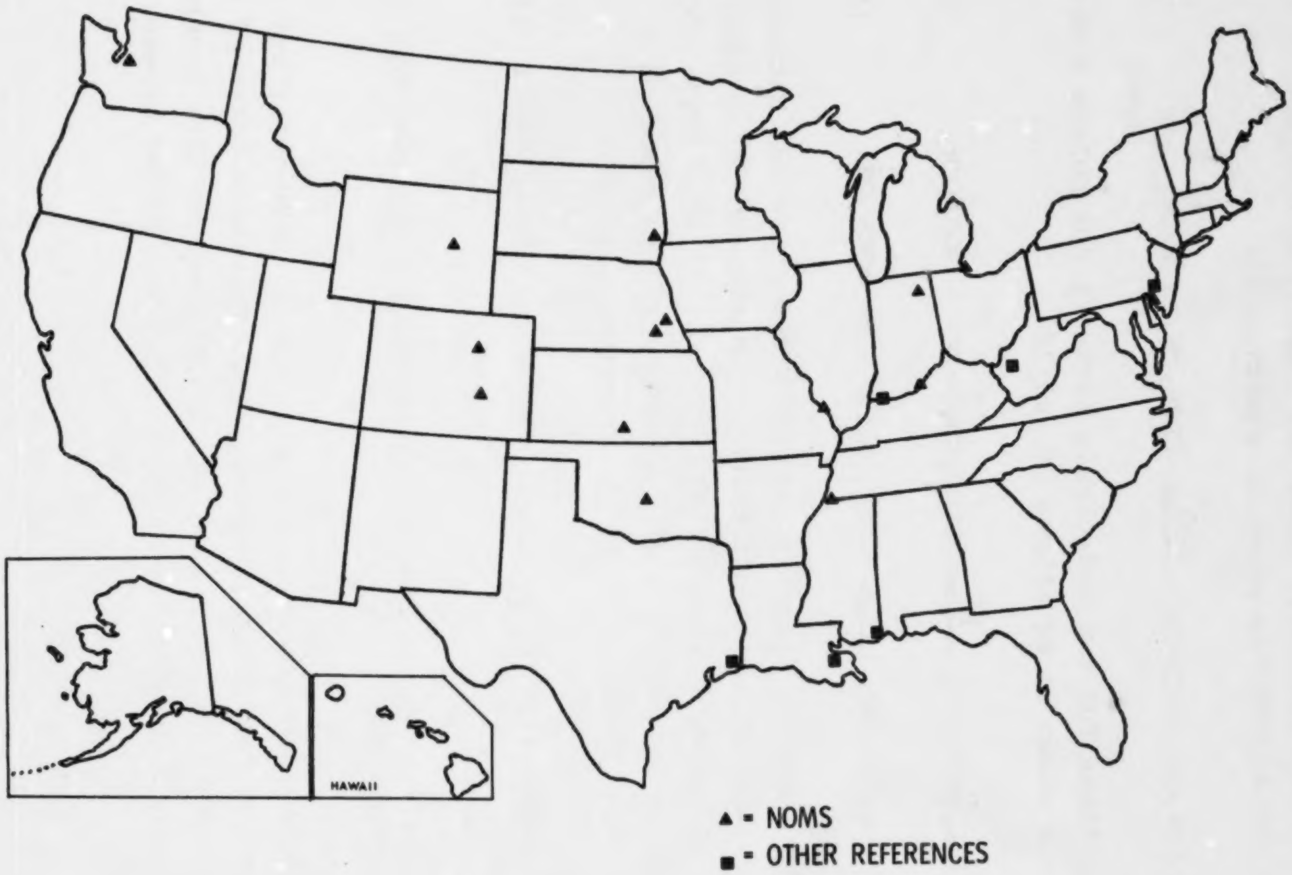
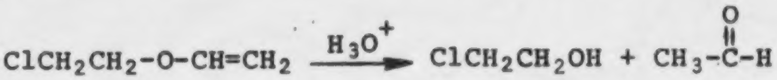

HAWAII
▲ = NOMS
■ = OTHER REFERENCES

Figure 2. Sites where β-Chloroethers have been found.

acetals under acid conditions. They found the chlorovinyl ethers such as chloroethyl vinyl ether are readily hydrolyzed to an aldehyde and alcohol as shown in equation 15.



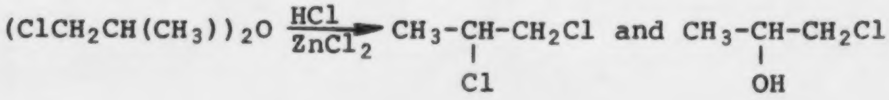
$$ClCH_2CH_2\text{-}O\text{-}CH{=}CH_2 \xrightarrow{H_3O^+} ClCH_2CH_2OH + CH_3\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}H \qquad (15)$$

Their equations for two hydrolysis pathways for chloro substituted acetals are shown in equations 16 and 17.

$$ClCH_2CH_2OCH_2 \vdots OCH_2CH_3 \xrightarrow{H^+} ClCH_2CH_2\overset{+}{O}{=}CH_2 + HOCH_2CH_3 \qquad (16)$$

$$ClCH_2CH_2 \vdots OCH_2OCH_2CH_3 \xrightarrow{H^+} ClCH_2CH_2OH + CH_2{=}\overset{+}{O}CH_2CH_3 \qquad (17)$$

As part of a hazard priority ranking program for the National Science Foundation, Stanford Research Institute (54) predicted a half life for BCEE in water at a pH of 7 of 38.2 days. One other process for catalytically cleaving BCIPE, based on a patent by Dow Chemical, is shown in equation 18 (55).



$$(ClCH_2CH(CH_3))_2O \xrightarrow[ZnCl_2]{HCl} CH_3\text{-}\underset{\underset{\displaystyle Cl}{|}}{CH}\text{-}CH_2Cl \text{ and } CH_3\text{-}\underset{\underset{\displaystyle OH}{|}}{CH}\text{-}CH_2Cl \qquad (18)$$

2.3 METHODS FOR THE ISOLATION, CONCENTRATION AND ANALYSIS OF β-CHLOROETHERS

The isolation, concentration and analysis methods described in the literature have been directed primarily toward three of the haloethers, BCEE, BCIPE and BCEXM, of interest to this program. Descriptions of the methods reported will be divided between air and water.

2.3.1 Air

Two main types of methods, direct analysis and use of sorbants, have been employed for collection and concentration of β-chloroethers. In addition, derivative formation has been used to collect bis(chloromethyl) ether (BCME) from air. These methods are included because it was felt early in this program that derivative formation might be a good method for β-chloroethers.

2.3.1.1 Direct Analysis--

Direct analysis for fumigant gases were performed by Berck (56) with a 1.8 m x 4 mm stainless steel column packed with 10% SE-30 on Diatoport S. The haloether analyzed for was BCEE and a thermal conductivity detector was used.

2.3.1.2 Sorbents--

A variety of sorbents have been used to collect β-chloroethers from air. The adsorbers are then thermally desorbed onto a gas chromatographic column, which is connected to a low or high resolution mass spectrometer. Table 9 cites the haloethers which were being collected, the sorbant used for collection, the gas chromatographic column employed and the reference number of the literature from which these data were taken.

A method based on absorbers for collection makes use of solvent for desorption purposes. NIOSH traps BCEE from work-place environments on charcoal. The BCEE is desorbed with carbon disulfide and analyzed by gas chromatography on 10% FFAP on 80/100 mesh acid-washed, DMCS-treated Chromosorb W (60).

2.3.1.3 Derivatives--

The third procedure used to collect and analyze BCME in air is based on derivative formation followed by gas chromatography with an electron capture detector. The derivatives are formed via the reaction in methanol solution between BCME being scrubbed

TABLE 9. ANALYSIS OF HALOETHERS IN AIR WITH SORBENT GAS CHROMATOGRAPHY/MASS SPECTROMETRY

β-chloroether	Sorbent	Gas chromatographic column	Reference
BCME,BCEE	Chromosorb 101 Chromosorb 104 Tenax GC Porapak Q Activated Carbons 20% Carbowax 600 on Chromosorb W Carbowax 400/Porsail C Oxypropionitrile/ Porasil C 25% Didecylphthlate on Chrom. P 20% Tricresyl Phosphate on Chrom. W	2% DEGS on Chromosorb W (HP) 80/100 mesh 3.6 m x 2.5 mm	57 58
BCME,BCEE	Tenax GC	Tenax GC (3.6 m x 2.5 mm) 2% DEGS on Supelcoport (80/100 mesh) (3.6 m x 2.5 mm)	59

from the air and the sodium salt of 2,4,6 trichlorophenol. Other sodium salts of alkyl or aryl oxides have been used by other workers. The materials used to form derivatives, the gas chromatographic column used for analysis and the references are listed in Table 10.

2.3.2 Water

The major methods of isolation and concentration of haloethers from water have centered around sorption on charcoal or solvent extraction. Method of analysis is primarily gas chromatography with different detectors.

Table 11 lists the method of isolation and concentration, the gas chromatography detector used, and the reference for haloethers in water. In addition to these standard techniques, Deinzer, et al. tested the use of a cellulose acetate reverse osmosis membrane for concentrating BCEE and BCIPE from water (65). They were not successful in increasing the concentration of these two compounds in the reject water with the membrane they were using.

TABLE 10. DERIVATIVE FORMATION FOR ANALYSIS FOR BCME IN AIR

Derivative reagent	Gas chromatographic column	Reference
Na 2,4,6-trichlorophenate	0.1% QF-1 and 0.1% OV-17 on 100/120 mesh textured glass beads (GLC 100) (1.8 m x 4 mm)	61
Na phenate Na methoxide Na ethoxide Na thiophenate Na 2,4,6-trichlorophenate	LAC-2R446 + 2% H_3PO_4	62
Na 2,4,6-trichlorophenate	-	63

TABLE 11. ANALYSIS OF HALOETHERS IN WATER

Haloethers	Isolation concentration technique	Gas chromatograph column	Detector	Reference
BCEE, BCIPE	Carbon chloroform extraction	-	IR	47
BCEE, BCIPE BCEXM	Solvent	4% FFAP on Chromosorb W (1.8mx2.1mm or 4mm)	FID, mass spec.	51
BCEE, BCIPE	Carbon chloroform extraction	5% SE-30 on Chromosorb W 60/80 mesh (1.8m x 2mm)	FID, mass spec.	49
	Extraction with 5% ethyl ether in hexane	5% OV-17 on Chromosorb W 60/80 mesh (1.8m x 2mm)		
BCEE, BCIPE	Extraction with 15% ethyl ether in hexane	4% SE-30 + 6% OV-210 on Gas Chrom. Q (1.8m x 2.1mm)	Microcoulometric, electrolytic conductivity	53
		3% SP 1000 on Supelecoport 100/120 mesh (1.8m x 2.1 mm)		
BCEM, CEVE	Purge and trap	0.2% Carbowax 1500 on Carbopak C (60/80 mesh) (2.4mx2.1mm) + Carbowax 1500 on Chromosorb W (0.3m x 2.1mm)	Mass spec.	64
BCIPE, BCEE	Methylene chloride extraction	1% SP 2250 on Supelecoport (100/120 mesh) (1.8m x 2mm)	Mass spec.	64
BCIPE, BCEE		OV-17 SCOT Column	Mass spec.	64

SECTION 3

SAMPLING SITE SELECTION

From information in the open literature we were able to determine 19 plant sites where the greatest concentrations of β-chloroethers are likely to be found. These plants, the β-chloroether expected, the chemical which is being produced and which could result in the β-chloroether emission, and the plant site are listed in Table 12. This list was then reviewed with regard to plant size, access and other information we were able to gather from state and local agencies. In addition EPA-OTS contacted Regional EPA personnel for recommendations as to plants in their region which were potential β-chloroether emitters. From these contacts the Milliken Chemical Company, Inman, S.C. was added to the original list of 19.

During the time we were sampling these industrial sites and analyzing the samples, the results of the NOMS survey were published (53). We were requested by EPA-OTS to contact the authors of the NOMS survey paper. From this contact it was learned that BCEE and BCIPE were found at Sioux Falls, S.D. Contacts with regional EPA personnel resulted in our sending cleaned amber jugs with Teflon-lined caps for use in sampling the Sioux Falls, S.D. water treatment plant effluent. Four samples were collected, shipped to MRC, extracted, concentrated and analyzed as described in Sections 4, 5 and 6. The samples were taken on August 13 and 14 and September 13 and 15, 1977. The September 15, 1977 sample was broken in transit. Four liters of each sample were extracted and neither BCEE nor BCIPE were detected in the remaining 3 samples.

TABLE 12. LIST OF PREFERRED SAMPLING SITES BY CATEGORIES

I. β -chloroether producers

Chemical	Company	Plant site
Bis(2-chloroethyl) ether	Buckman Labs., Inc.	Cadet, Missouri Memphis, Tennessee
Bis(2-chloroisopropyl) ether	Dow Chemical USA	Freeport, Texas

II. β-chloroethers as by-products

Chemical	Chemical produced	Company	Plant site
Bis(2-chloroethyl) ether	Ethylene chlorohydrin	Union Carbide Corp.	Institute & S. Charleston, W. Virginia
Bis(2-chloroiso-propyl) ether	Propylene chlorohydrin	Eastman Kodak	Rochester, N.Y.
		RSA Corp.	Ardsley, N.Y.
	Propylene oxide	BASF Wyandotte Corp.	Wyandotte, Mich.
		Dow Chemical USA	Freeport, Texas Plaquemine, La.
		Olin Corp.	Brandenburg, Ky.
		Oxirane Corp.	Bayport, Texas
		Texaco, Inc.	Port Neches, Texas
	Propylene glycol	Dow Chemical USA	Plaquemine, La. Freeport, Texas
		Olin Corp.	Brandenburg, Ky.
		Oxirane Corp.	Bayport, Texas
		Texaco, Inc.	Port Neches, Tx.
		Union Carbide Corp.	Institute & S. Charleston, W. Virginia
Bis(1-chloromethy, 2-chloroethyl) ether	Epichlorohydrin	Dow Chemical USA	Freeport, Texas
		Shell Oil Co.	Deer Park, Tx. Norco, Pa.

III. β-chloroether users

Bis(2-chloroethoxy) methane	Polysulfide polymers	Diamond Shamrock	Ashtabula, Ohio
		The Flame Master Corp.	Sun Valley, Ca.
		Product's Research & Chem. Corp.	Gloucester City, New Jersey Glendale, Ca.
		Sybron Corp.	Romulus, Mich.
		Thiokol Corp.	Moss Point, Miss.

The detection limit for BCEE and BCIPE in the samples was 3×10^{-8} g/l.

After this process a final list of eight plants was chosen by EPA-OTS. The plants sampled are listed in Table 13. The plant locations are shown graphically on a map of the United States in Figure 3. The numbers shown are also the order in which the plants were sampled.

TABLE 13. PLANT SITES FOR β-CHLOROETHER SAMPLING AND ANALYSIS

Company	Plant Site	Number on Figure 3
Olin Corporation	Brandenburg, Kentucky	1
Dow Chemical USA	Freeport, Texas	2
Jefferson Chemical	Port Neches, Texas	3
Dow Chemical USA	Plaquemina, Louisiana	4
Thiokol Corporation	Moss Point, Mississippi	5
Union Carbide Corporation	Institute, West Virginia	6
Milliken Chemical	Inman, South Carolina	7
Eastman Kodak	Rochester, New York	8

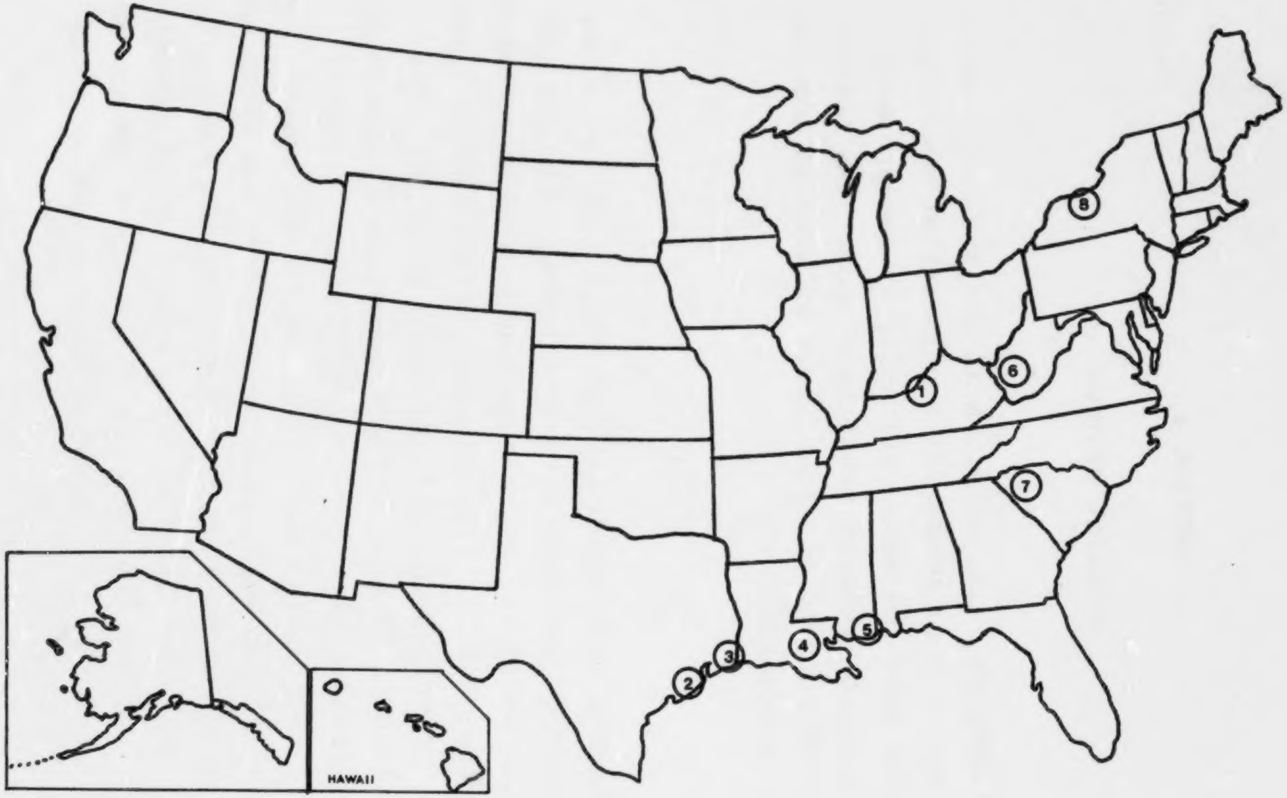

8
6
1
7
5
4
3
2
HAWAII

Figure 3. β-chloroethers sampling sites.

SECTION 4

SAMPLING METHODS

Four types of samples, air, water, soil and sediment, were taken in the vicinity of potential β-chloroether producing plants. Samples were collected primarily on public lands; at no time was plant property trespassed upon. The methods used for sampling each of the four types of samples are described in this section.

4.1 AIR

Ambient air samples were drawn through Pyrex sampling tubes packed with Tenax-GC and then through a backup charcoal sampling tube with Bendix Model 115 and 130 samplers. Air flow through the sampling tubes was 1.0 liter/minute. Air sampling times were ∿8 hours during daylight and ∿12 hours at night. The largest concentration of samplers was placed in an arc in the predominant downwind direction from the plants. Normally 8 samplers were used during daylight. Six of the samplers were placed downwind and two were placed upwind from the plant complexes. During the night 2 or 3 samplers were employed with 1 upwind and 1 or 2 downwind from the plant. The air samplers were mounted on 1.25 cm diameter rods 1.5 m above the ground level. A typical air sampler mounting arrangement is shown schematically in Figure 4.

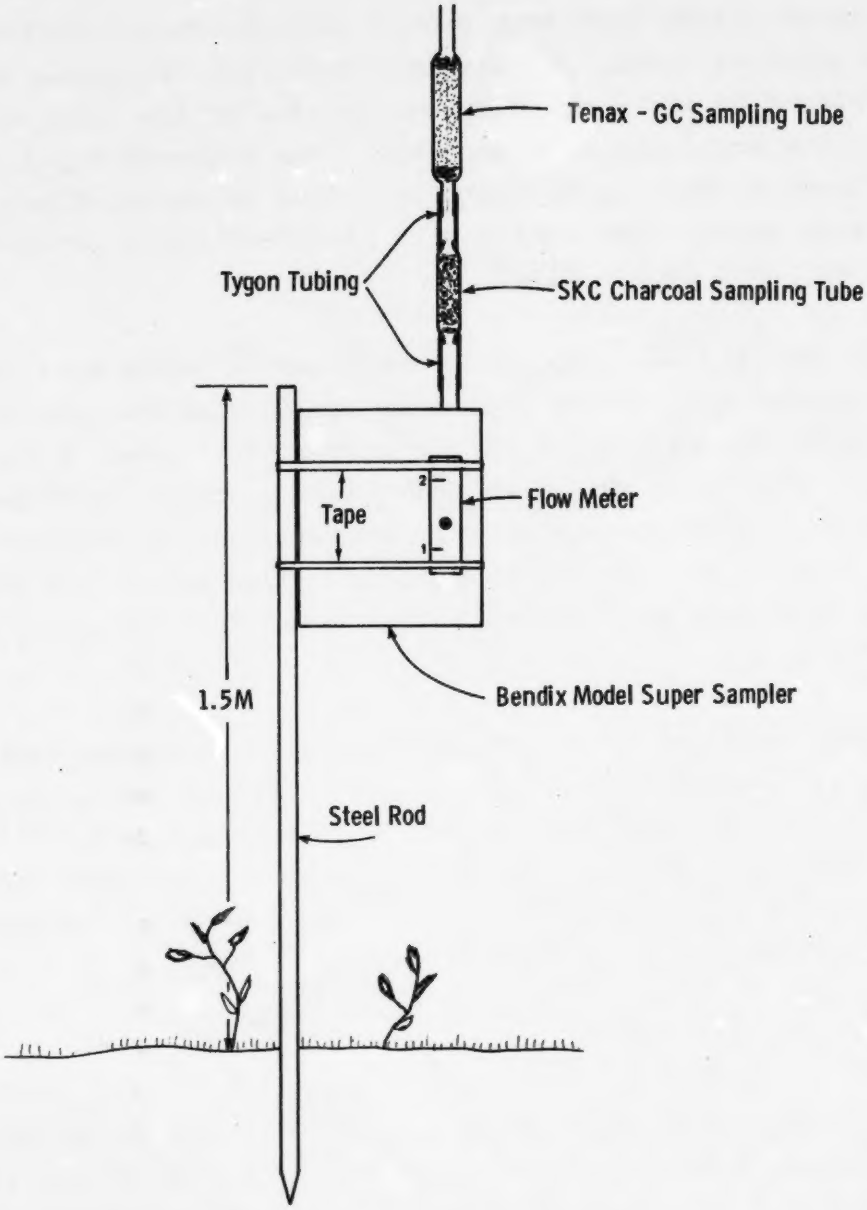

Tenax - GC Sampling Tube
Tygon Tubing
SKC Charcoal Sampling Tube
2
Tape
Flow Meter
1
1.5M
Bendix Model Super Sampler
Steel Rod

Figure 4. Air sampler arrangement.

The sampling tubes which were packed with Tenax-GC are shown schematically in Figure 5. Approximately 2.5-3.0 grams of Tenax-GC (60/80 mesh) were packed into the center portion of the sampling tubes. It was important that the glass wool plugs be placed in the large diameter portion of the tube so the air flow would not be restricted. The Tenax-GC tubes were conditioned by heating to 300°C in a flow of oxygen-free nitrogen for sixteen hours, then sealed with stainless steel Swagelok caps for shipment to the field.

When sampling was completed, the Tenax-GC tubes were removed and sealed with either stainless steel Swagelok caps or with polyethylene caps which slip over the glass ends of the sampling tube. The tubes were then individually wrapped with paper towels to protect them against breakage during shipment by air freight back to the laboratory. Upon arrival at the laboratory the tubes were stored in a freezer at -20°C until time for sample workup.

At each site one unused Tenax-GC sampling tube was doped with $\sim 2 \times 10^{-5}$ grams of each of the six β-chloroethers. An additional unused sampling tube was also retained as a control for the doped sample. Doped and control tubes were treated in exactly the same manner as sample tubes during shipment, storage, workup and analysis.

4.2 WATER

Twenty-four-hour water samples were collected at two points downstream from the potential β-chloroether producing plant's outfall and at one point upstream. The water samples were taken 1.8 m from the bank of the stream being sampled and 20 cm below the water surface. The sampling system used is shown schematically in Figure 6. Samples were drawn through Tygon tubing by a peristaltic pump. The end of the sampling

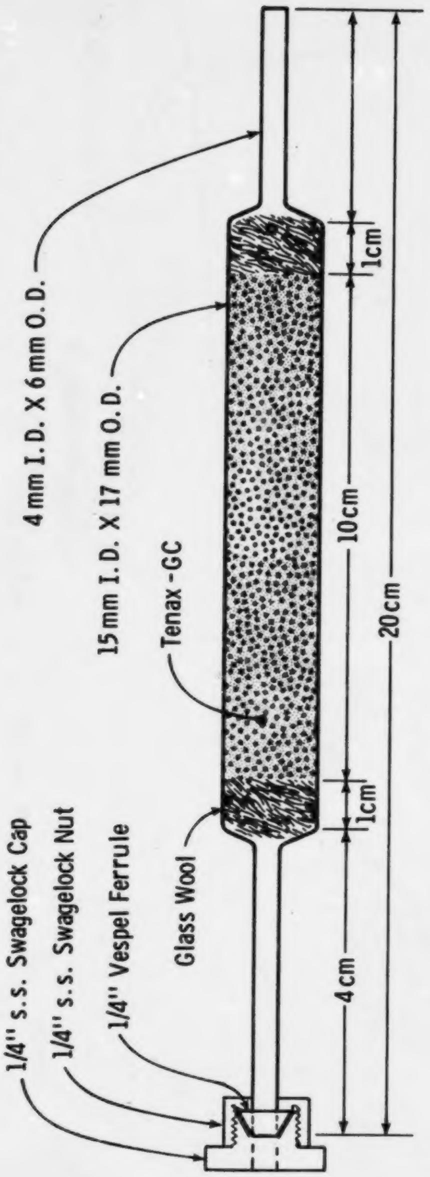

1/4" s.s. Swagelock Cap
1/4" s.s. Swagelock Nut
1/4" Vespel Ferrule
Glass Wool
Tenax-GC
15 mm I.D. X 17 mm O.D.
4 mm I.D. X 6 mm O.D.
4 cm
1 cm
10 cm
1 cm
20 cm

Figure 5. Pyrex sampling tube packed with Tenax-GC.

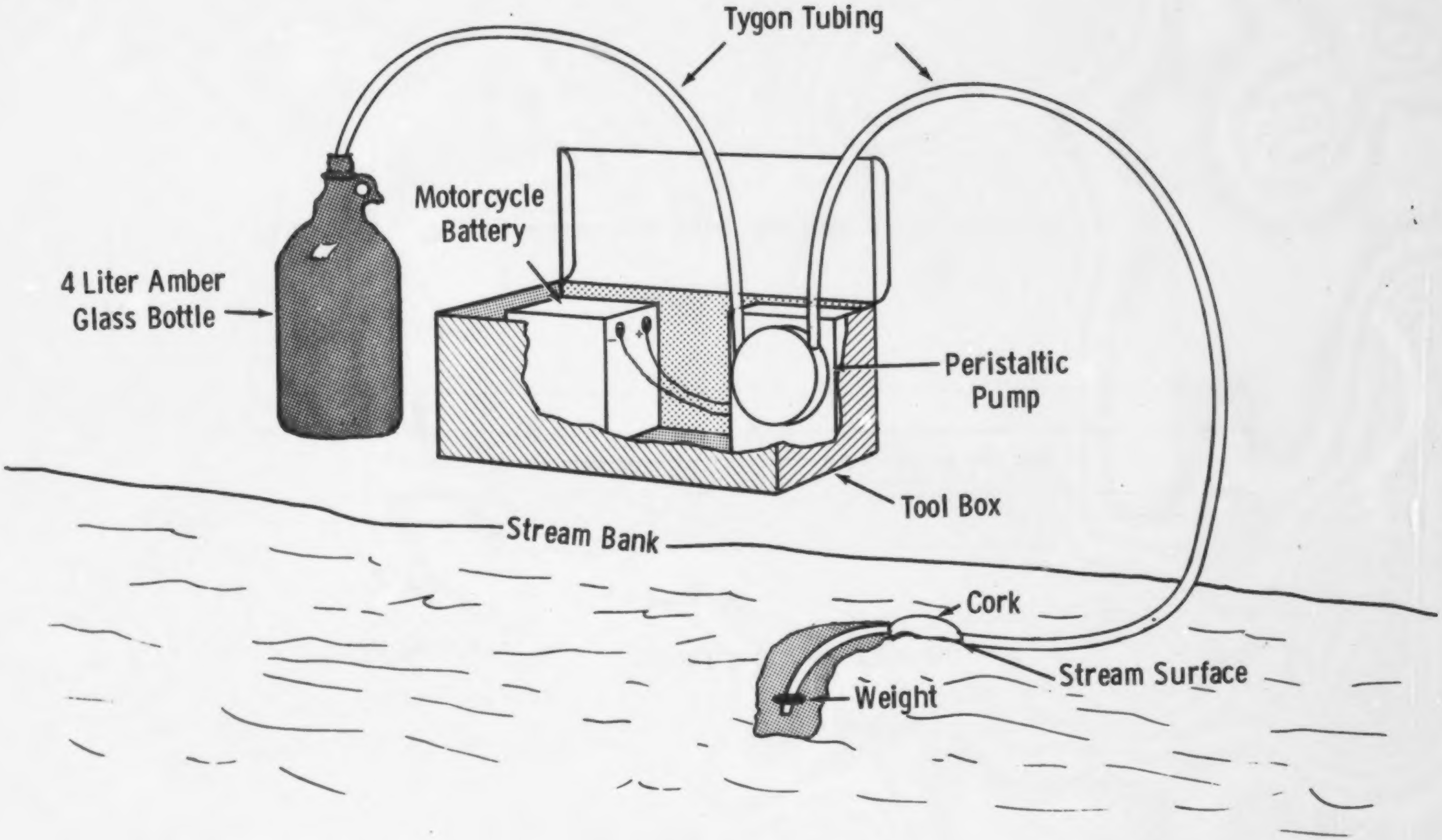

Tygon Tubing
Motorcycle Battery
4 Liter Amber Glass Bottle
Peristaltic Pump
Tool Box
Stream Bank
Cork
Stream Surface
Weight

Figure 6. Water sampler arrangement.

tube was held up off the bottom by a cork float and below the water line by a weight. The peristaltic pump was powered by a motorcycle battery. Both the battery and pump were housed in a metal toolbox. The water flowed through the pump into a 4 liter amber glass bottle at a rate of 166 cm^3/hr. The amber glass bottles used were purchased from Burdick-Jackson, Muskegon, Michigan and had been cleaned and dried by Burdick-Jackson. These bottles are the same as those bottles used by Burdick-Jackson for their distilled-in-glass solvents. The bottles were supplied with screw caps with Teflon liners.

After sampling, a small amount of sample was removed to allow for volume expansion and the caps were screwed onto the bottles. The caps were then sealed with plastic tape to prevent their working loose during shipment. The bottles containing the water samples were then wrapped with foam padding and placed in a large picnic ice chest. Remaining space in the ice chests was filled with ice and the chests were sealed with tape for shipment back to the laboratory by air freight. Upon arrival at the laboratory the samples were kept at 4°C until analyzed.

Two additional 1-liter samples were taken at the upstream sampling point. One sample was doped with $\sim 2 \times 10^{-5}$g of each of the β-chloroethers. The other 1-liter sample was labeled as a control. These two samples were subjected to the same packing, shipment, storage, extraction, concentration, and analysis procedures as were used for the water samples. These doped samples were to serve as checks for our methods and to indicate whether any biological degradation was occurring during shipment and storage before the water samples were extracted.

4.3 SOIL

Soil samples were taken at various points around the sites of the potential β-chloroether producing plants. One soil sample was taken at each air sampling site. Additional soil samples were taken in the directions of the points of annual wind rose charts. Where applicable, samples were also taken in areas of maximum population density surrounding the sites.

Soil samples were collected using tulip bulb planters. The vegetation in the area was removed and a core ∿ 6 cm in diameter by 7.5 cm in depth taken. The core was then placed in a wide-mouthed canning jar (∿ 500 cm^3 capacity). The jar lid was then replaced and the sealing ring tightened. Sample numbers were scribed on the lids of the jars. Each jar was then wrapped with duct tape to insure retention of the sample even if the glass jar broke during shipment. The jars were then returned to their original boxes and when the boxes were filled, they were sealed and air freighted back to the laboratory.

Two additional soil samples were taken at a point where maximum deposition of compounds of interest could occur. One sample was doped with $\sim 2 \times 10^{-5}$g of each of the β-chloroethers and the other sample was held as a control. The recovery results of the doped sample were checked against recovery data for samples which had been doped in the laboratory.

4.4 SEDIMENT

Sediment samples were taken at selected downstream locations at each site. The samples were collected with a collapsible shovel, approximately 0.5 meter from the bank of the stream. The samples were transferred from the shovel to canning jars and treated in the manner described for the soil samples.

SECTION 5

SAMPLE WORKUP METHODS

This section describes the procedures used to recover the β-chloroethers from the samples which were collected at the field sites.

5.1 AIR

All but two of the Tenax-GC sampling tubes from each site were solvent desorbed with methanol. The remaining two samples (normally one from a potentially high concentration site sampled during the day and one sample collected at night) were held for complete characterization via thermal desorption and gas chromatography/mass spectrometry.

The apparatus used for solvent desorption is shown in Figure 7. Approximately 4 cm^3 of methanol was pumped through the Tenax-GC sampling tube in the opposite direction of the air flow during sampling. The methanol was collected in a tared vial and the vial was reweighed after desorption from each tube. The vials were capped with Viton septa and held for analysis. Analysis was performed by gas chromatography/mass spectrometry. The mass spectrometer was operating in the selected ion mode (SIM).

5.2 WATER

One liter from each water sample was extracted three times in a separatory funnel with 100 cm^3 of methylene chloride. The methylene chloride extracts were combined and evaporated using a Kuderna-Danish evaporator to a volume of 1-2 cm^3. The solu-

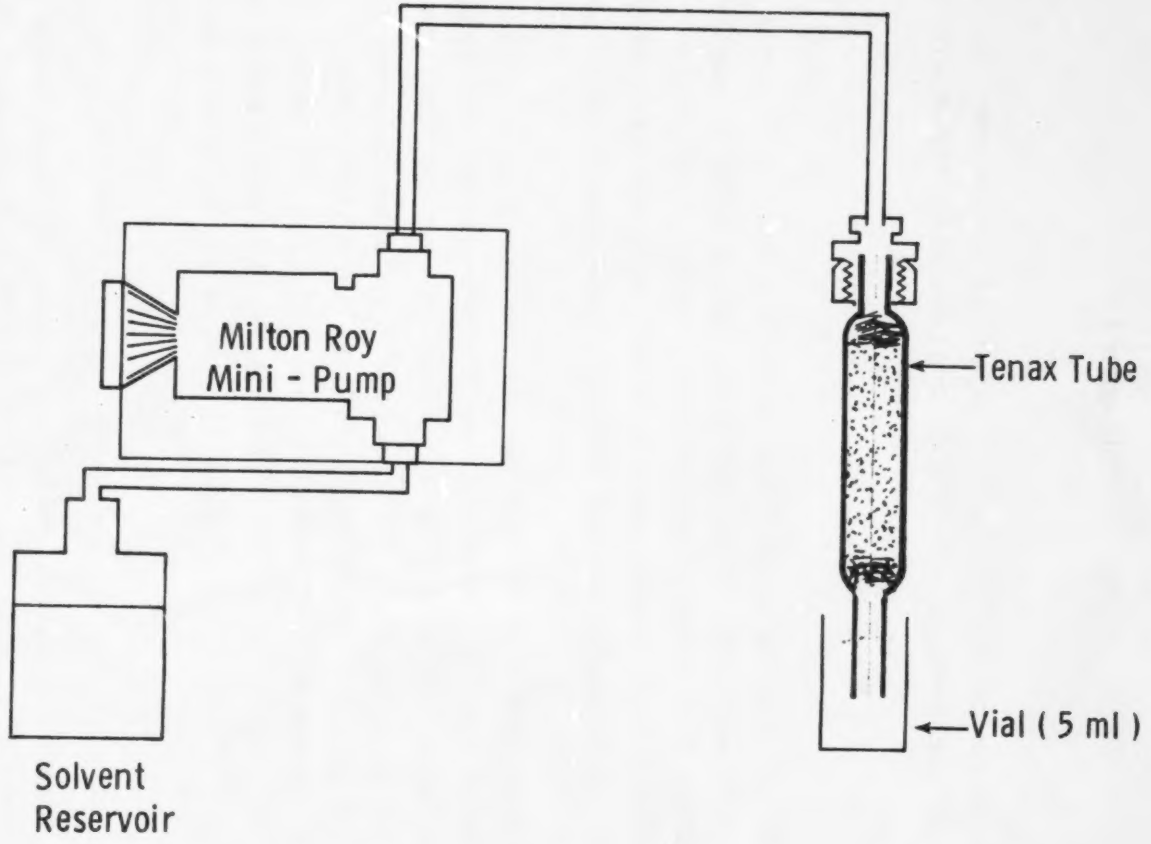

Milton Roy
Mini - Pump
Tenax Tube
Vial (5 ml)
Solvent
Reservoir

Figure 7. Solvent desorption apparatus.

tion remaining in the receiver was then transferred to a tared vial and the Kuderna-Danish apparatus rinsed with small portions of methylene chloride. These rinses were then transferred to the vial and a Viton spectum cap replaced on the vial. The vials were then reweighed. The samples were held for subsequent GC-MS-SIM analysis.

5.3 SOIL

Five soil samples from each site were selected. Approximately 50 g of each sample was transferred to an extraction cup. The samples were then extracted in a Soxhlet apparatus for ∿ 16 hours. Approximately 200 cm^3 of methylene chloride was used for the extractions. After cooling, the methylene chloride extracts were then transferred to Kuderna-Danish evaporators and concentrated to ∿ 1-2 cm^3. Again the Kuderna-Danish apparatus was rinsed and the washings were combined with the concentrated solution in tared vials. The vials were sealed with Viton septa and reweighed. The samples were then held for analysis via GC-MS-SIM.

5.4 SEDIMENT

Sediment samples were treated in exactly the same way as described for soil samples except slightly larger samples were taken because of water content and samples were weighed before and after extraction.

SECTION 6

ANALYTICAL METHODS

This section concerns the methods used to analyze the samples collected and worked up as described in the two previous sections. Subsection 6.1 is devoted to the six haloethers of primary interest. Subsection 6.2 is a description of efforts to synthesize bis(1-chloromethyl,2-chloroethyl) ether and to simulate the synthesis of epichlorohydrin. Subsection 6.3 is a listing of the other compounds related to the haloethers for which selected samples were examined. Finally, in Subsection 6.4, methods are described which were used to perform complete characterization of at least one water sample and one air sample from each site.

6.1 SIX β-CHLOROETHERS

Analyses of the samples described in the sampling and workup sections were performed via gas chromatography/mass spectrometry. The mass spectrometer was operated in the selected ion mode (SIM) so maximum sensitivity could be achieved. The six β-chloroethers being quantitated in the samples, their abbreviations, and their characteristic ion pairs are listed in Table 14.

Before the analysis of the samples by SIM, a high concentration standard was run with the mass spectrometer operating in a scanning mode. Table 15 lists the instrumental conditions we used to run β-chloroether standards and samples. The total ion chromatogram obtained from the scanned run is shown in Figure 8.

TABLE 14. β-CHLOROETHERS ANALYZED FOR BY GC/MS/SIM

Compound	Abbreviation	Source*	Catalogue No.	Purity %	Masses
2-chloroethylvinyl ether	CEVE	Aldrich	10,998-3	99	63,106
2-chloroethylethyl ether	CEEE	Aldrich	C,4120-7	96	59,108
bis(2-chloroethyl)ether	BCEE	Matheson, Coleman & Bell	BX675		93,63
bis(2-chloroisopropyl)ether	BCIPE	Aldrich	S44368-9		45,121
bis(2-chloroethoxy)methane	BCEXM	Pfaltz & Bauer	B12370		93,63
bis(2-chloroethoxy)ethane	BCEXE	Pfaltz & Bauer	B12450		63,93

*Aldrich Chemical Company, 940 W. Saint Paul Avenue, Milwaukee, Wisconsin 53233
Matheson, Coleman & Bell, 2902 Highland Avenue, Norwood, Ohio 45212
Pfaltz & Bauer, 375 Fairfield Avenue, Stamford, Connecticut 06902

TABLE 15. GAS CHROMATOGRAPH/MASS SPECTROMETER CONDITIONS FOR β-CHLOROETHER ANALYSIS

Instrument: Hewlett-Packard Model 5983 GC/MS/DS

Column: 1.82 m x 0.21 mm (I.D.) glass packed with Tenax-GC (60/80 mesh)

Injection Port Temperature: 280°C

Transfer Line Temperature: 280°C

Column Temperature Programming: From 140°C to 260°C at 8°C/min. Hold at 260°C for 5 minutes.

Helium Flow Rate: 30/ml/min

Ion Source Temperature: 150°C

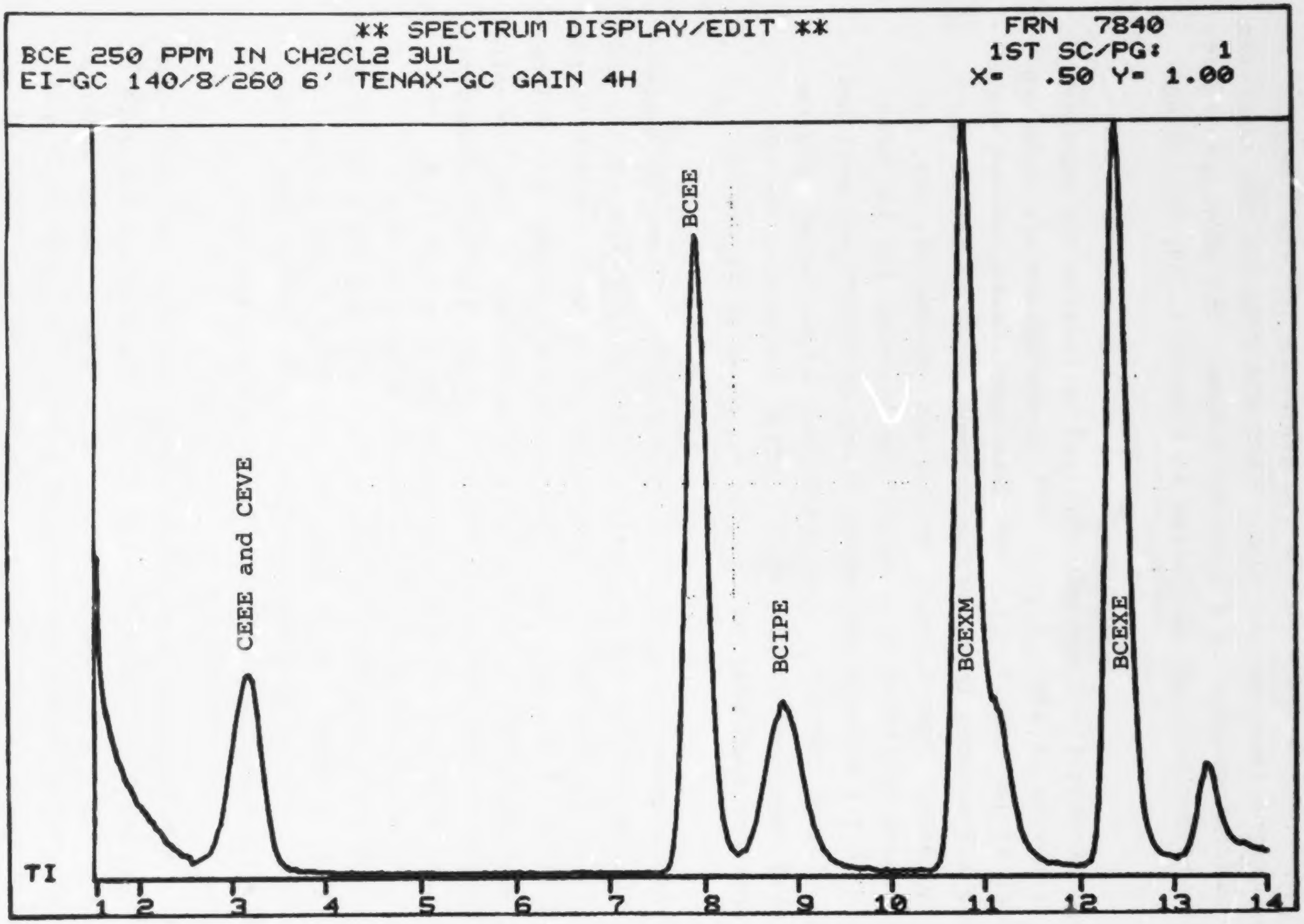


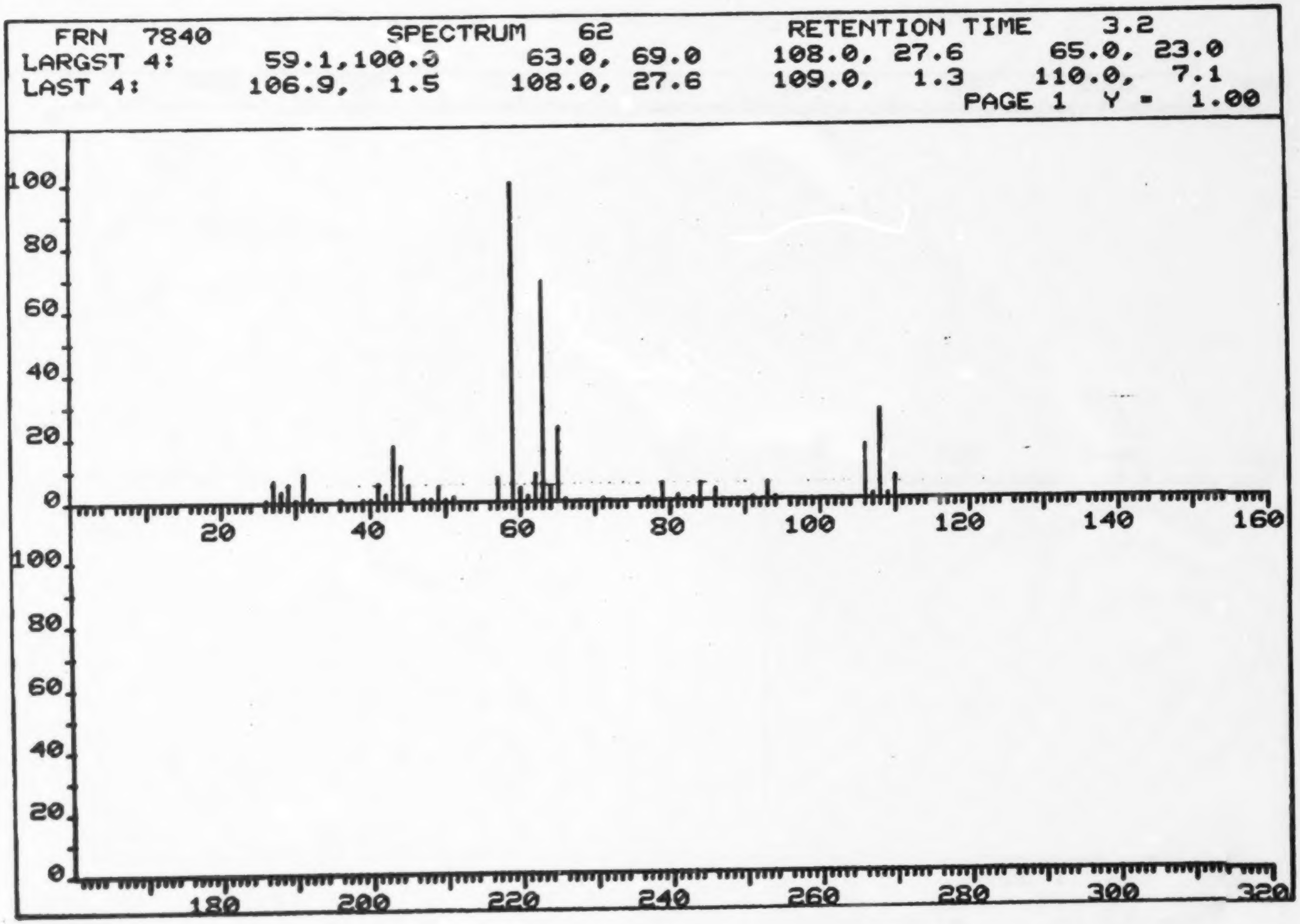
Figure 8. Total ion chromatogram of β-chloroethers

Each peak is labeled with the abbrevaiation for the compound or compounds found in the peak. CEVE and CEEE are not separated when chromatographed on a Tenax-GC column. The mass spectra for the β-chloroethers are displayed in Figures 9, 10, 11, 12 and 13.

Actual quantitative data were obtained by running the samples and standards in SIM. Typical SIM chromatograms are shown in Figures 14 (a) and 14 (b). The mass spectrometer was not turned on for 1.5 minutes to allow the solvent to clear before recording data. From 1.5 min. to 7.0 min. masses 59, 108, 63 and 106 were monitored in a repetitive sequence for 250 msec. each. At 7.0 minutes the masses being monitored were switched to 93, 63, 45 and 121. Again each mass was monitored in a repetitive sequence for 250 msec. After completing the run, the area for each mass was measured as shown in Figure 14.

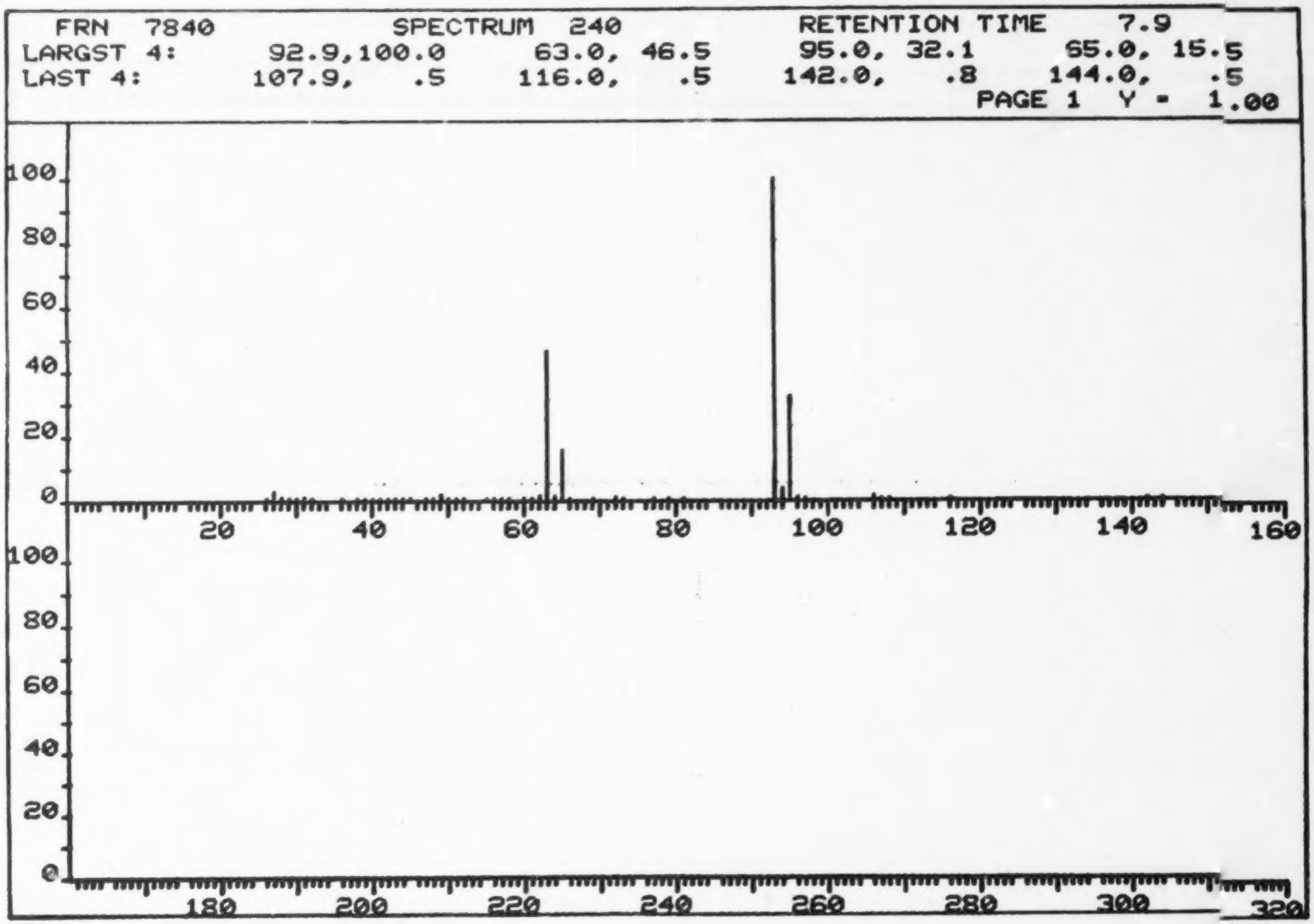
An average detection limit using the sample collection, extraction, concentration, and analysis methods was calculated for the four types of samples. The detection limits were subject to the variability of the mass spectrometer on a given day, the volume of sample collected or extracted, and the volume of the concentrated sample. Even when these variables were taken into consideration, the detection limits only varied by a factor of 4. The average detection limit for the β-chloroethers of the mass spectrometer operating in the SIM mode was 8.5×10^{-11} g/μl of sample injected. This detection limit was taken as the amount of material required to give a peak with an area three times the area of a blank run over the same time span.

For air samples the average detection limit was 7.0×10^{-7} g/m^3 (0.12 ppb) for samples collected during the day and 3.9×10^{-7} g/m^3 (0.07 ppb) for samples collected at night. Water samples had an average detection limit of 2×10^{-7} g/liter (0.2 ppb). Soil and sediment samples had an average detection limit of 4.1×10^{-9} g/g (4 ppb).



```
  FRN  7840            SPECTRUM    62              RETENTION TIME     3.2
LARGST 4:      59.1,100.0       63.0, 69.0      108.0, 27.6      65.0, 23.0
LAST 4:       106.9,   1.5     108.0, 27.6      109.0,  1.3     110.0,  7.1
                                                            PAGE 1   Y =  1.00
```

Figure 9. Mass spectra of 2-chloroethyl vinyl ether and 2-chloroethyl ethyl ether (CEVE and CEEE).



```
 FRN  7840            SPECTRUM  240              RETENTION TIME     7.9
LARGST 4:      92.9,100.0       63.0, 46.5      95.0, 32.1      65.0, 15.5
LAST 4:        107.9,    .5     116.0,    .5    142.0,    .8    144.0,    .5
                                                              PAGE 1  Y =  1.00
```

Figure 10. Mass spectrum of bis(2-chloroethyl)ether.

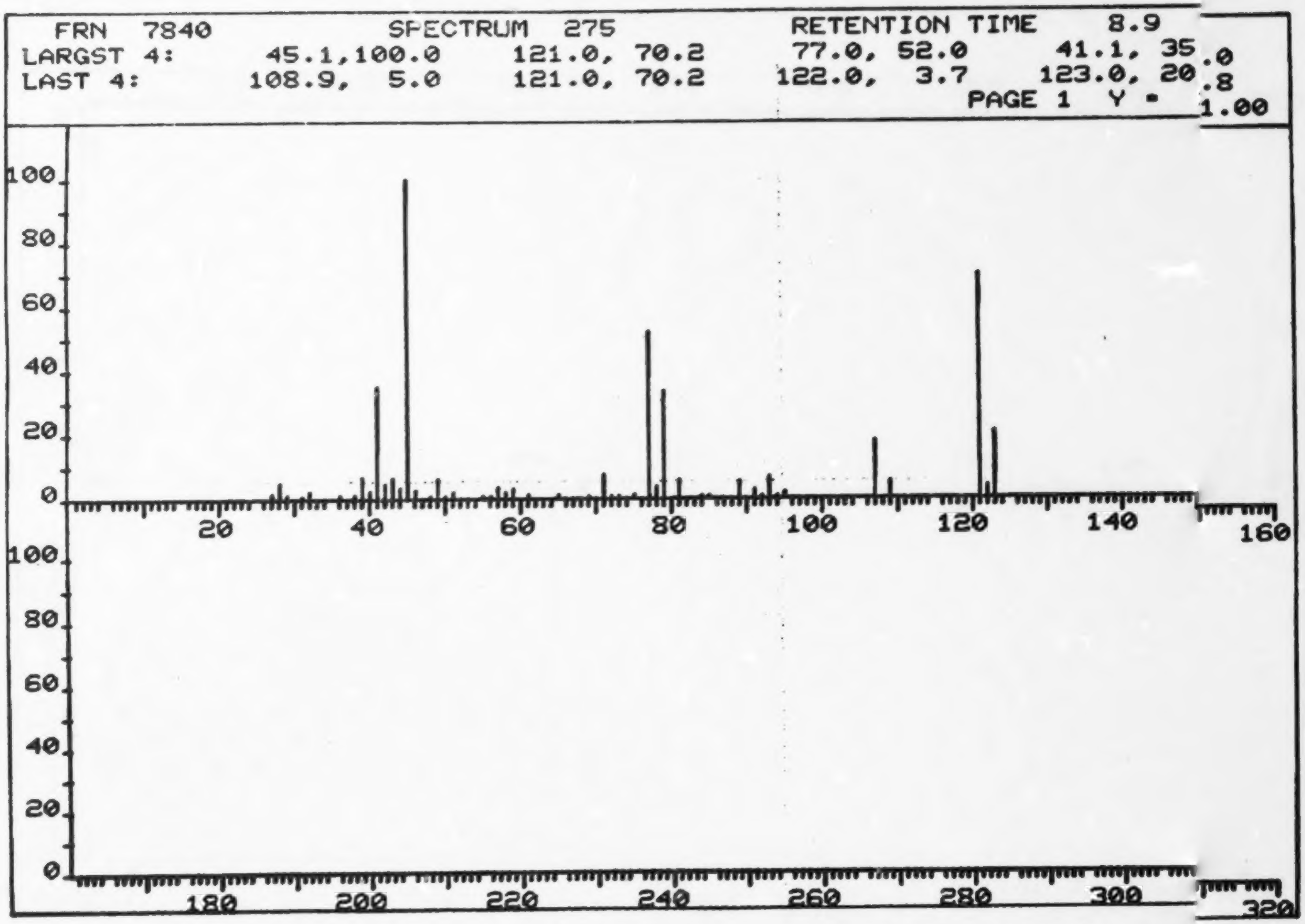


Figure 11. Mass spectrum of bis(2-chloroisopropyl)ether (BCIPE).

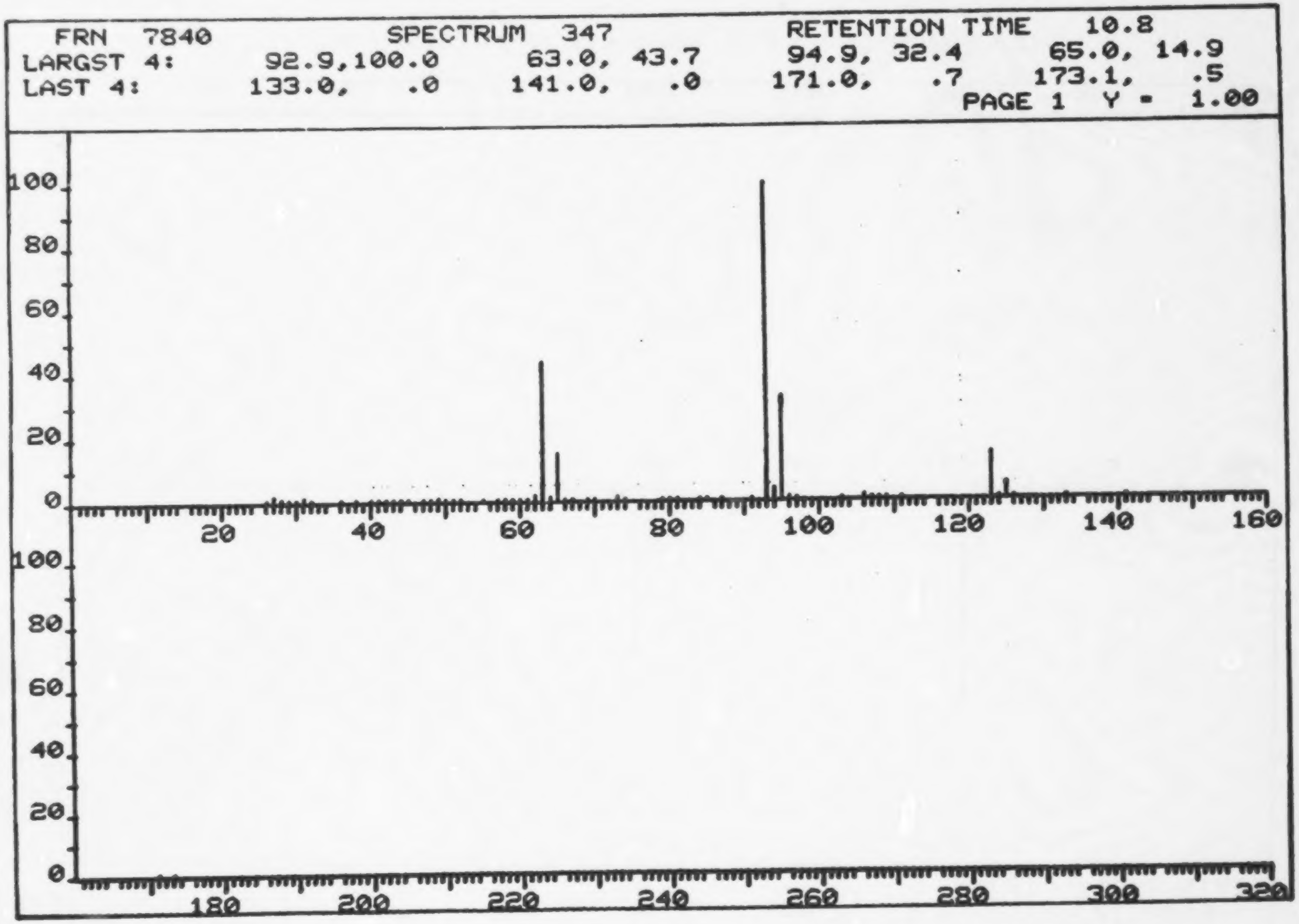


Figure 12. Mass spectrum of bis(2-chloroethoxy)methane (BCEXM).

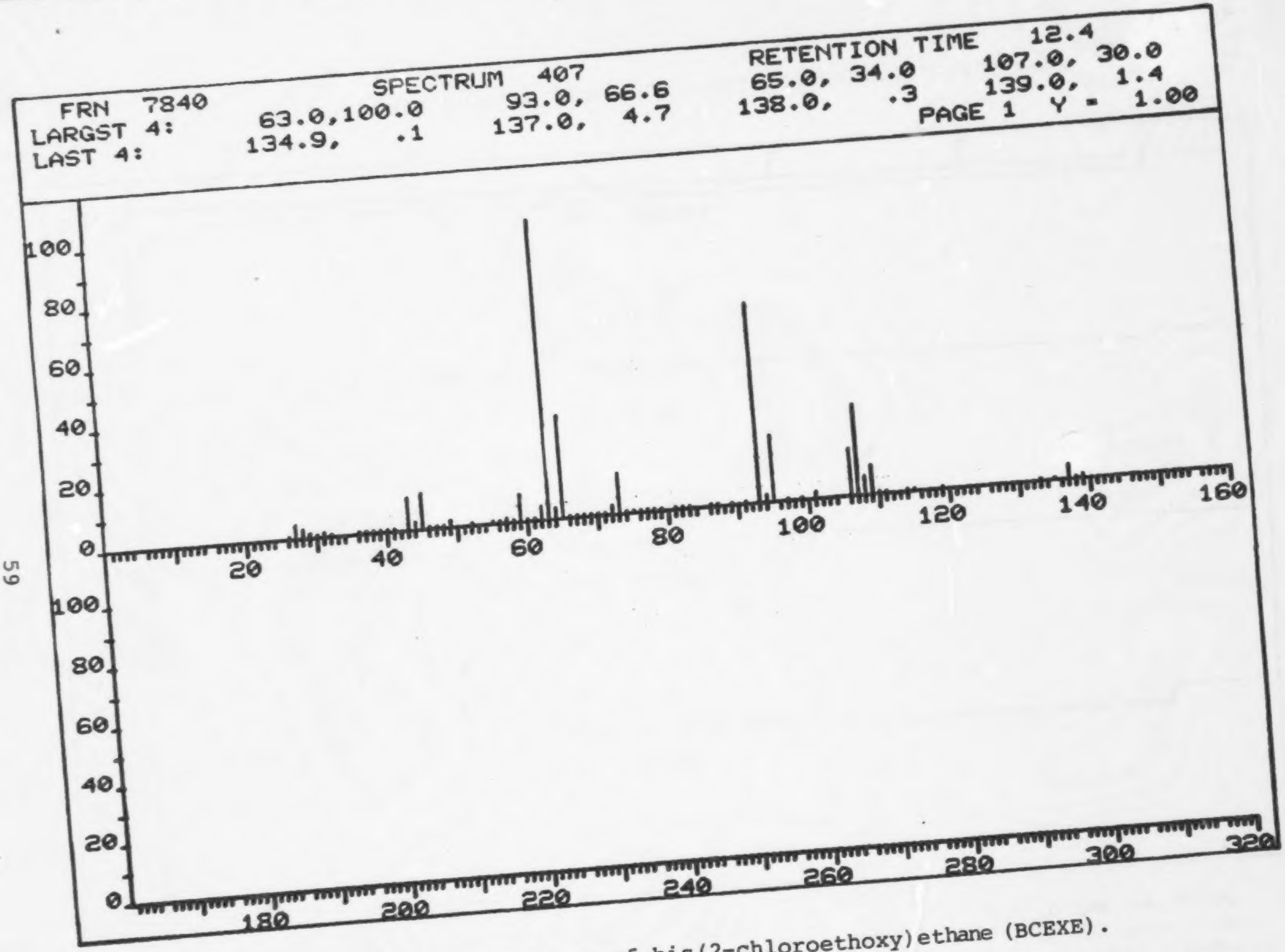


Figure 13. Mass spectrum of bis(2-chloroethoxy)ethane (BCEXE).

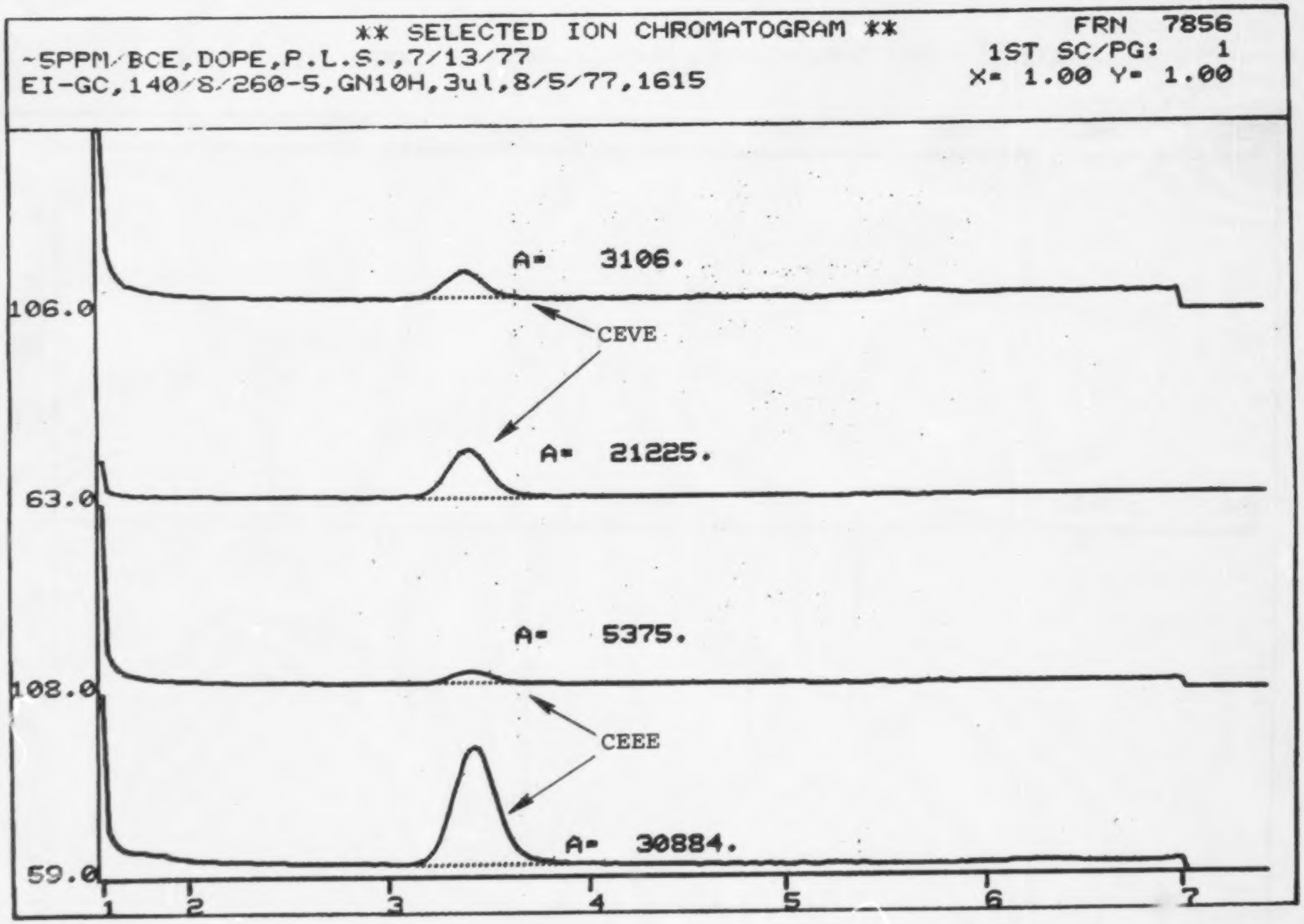


Figure 14 (a). SIM chromatograms for β-chloroethers (1.5-7.5 min).

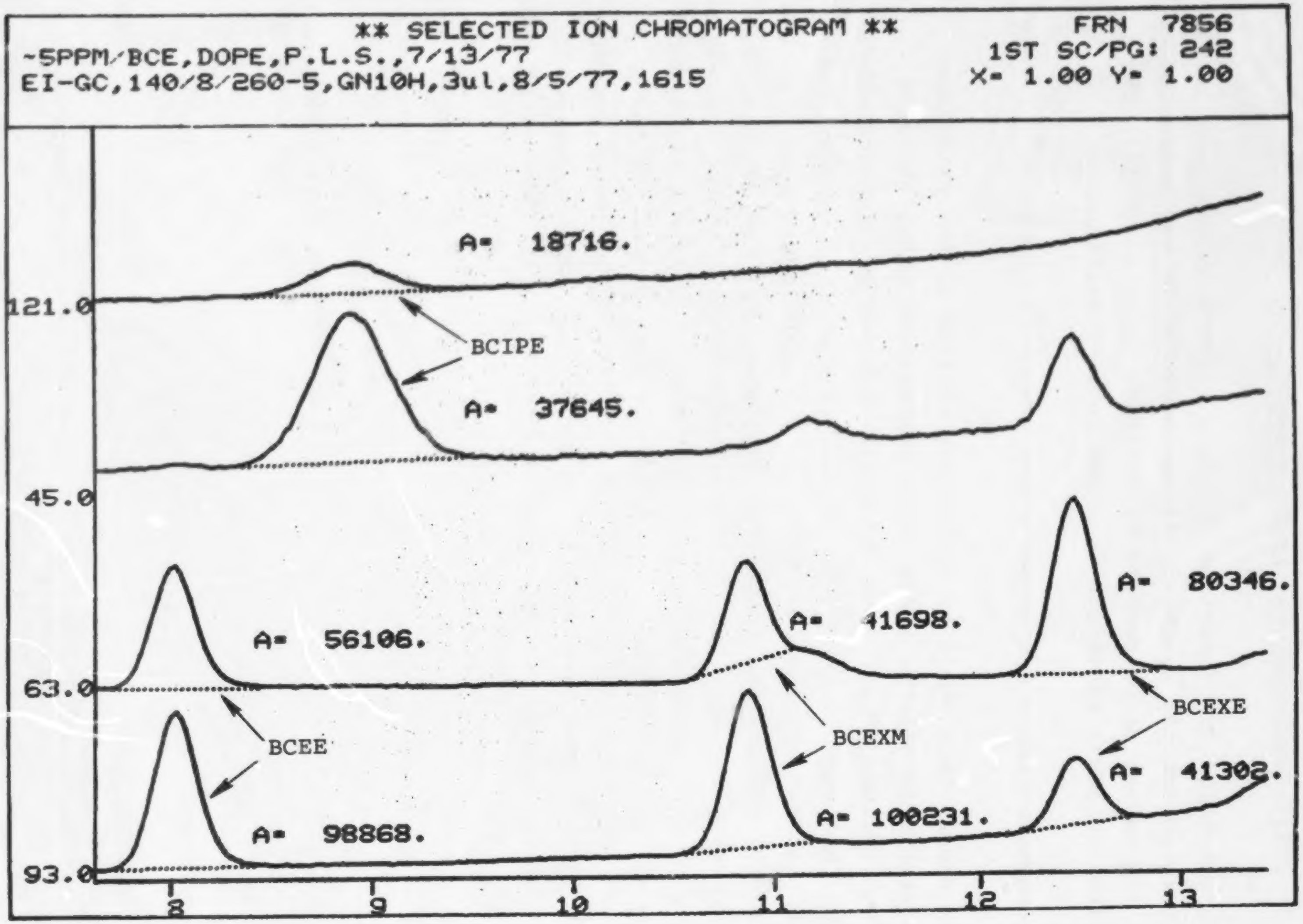
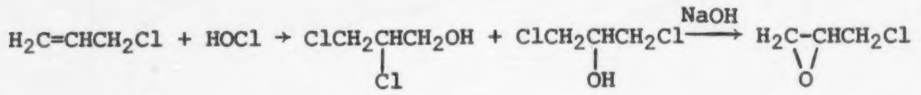


Figure 14 (b). SIM chromatograms for β-chloroethers (7.5-13.5 min).

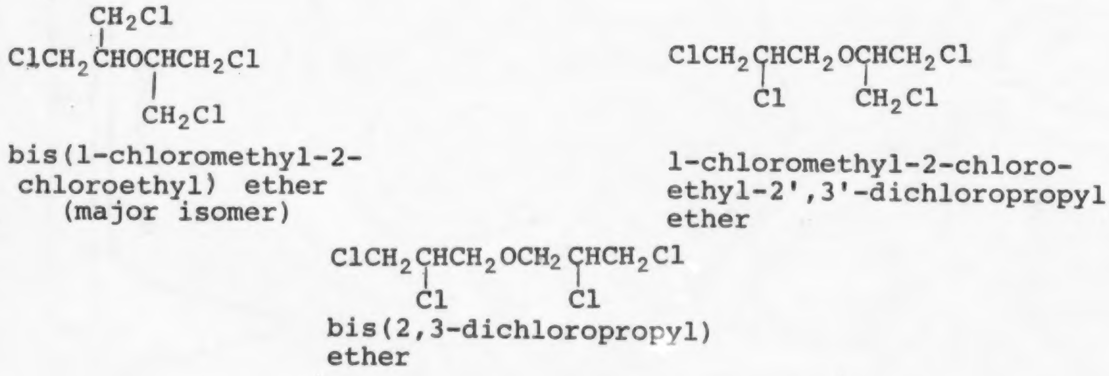
6.2 BIS(1-CHLOROMETHYL-2-CHLOROETHYL) ETHER

The potential for formation of three di-beta chloro substituted ethers during the synthesis of epichlorohydrin was suggested in the review on haloethers by Syracuse University (1). The epichlorohydrin synthesis is shown in this equation:



$$H_2C{=}CHCH_2Cl + HOCl \rightarrow ClCH_2\underset{Cl}{\underset{|}{C}}HCH_2OH + ClCH_2\underset{OH}{\underset{|}{C}}HCH_2Cl \xrightarrow{NaOH} H_2C\underset{\diagdown O \diagup}{-}CHCH_2Cl \qquad (18)$$

The ethers that could be formed are similar to the propylene chlorohydrin ethers, except they contain two extra chlorine atoms (Figure 15). Since the bis(1-chloromethyl-2-chloroethyl) ether and the other two ethers could be present in some of the samples taken during this contract and since these ethers are not commercially available, EPA-OTS suggested that MRC attempt to synthesize the bis(1-chlormethyl-2-chloroethyl) ether. In addition we were requested to simulate in the laboratory the synthesis of epichlorohydrin. The synthesis method used for bis-(1-chloromethyl-2-chloroethyl) of epichlorohydrin ether and epichlorohydrin are described in sections 6.2.1 and 6.2.2. The synthesis experiments were performed by Dr. A. Y. Gardner of MRC.



$$ClCH_2\overset{CH_2Cl}{\overset{|}{C}}HO\underset{CH_2Cl}{\underset{|}{C}}HCH_2Cl$$

bis(1-chloromethyl-2-chloroethyl) ether
(major isomer)

$$ClCH_2\underset{Cl}{\underset{|}{C}}HCH_2O\underset{CH_2Cl}{\underset{|}{C}}HCH_2Cl$$

1-chloromethyl-2-chloroethyl-2',3'-dichloropropyl ether

$$ClCH_2\underset{Cl}{\underset{|}{C}}HCH_2OCH_2\underset{Cl}{\underset{|}{C}}HCH_2Cl$$

bis(2,3-dichloropropyl) ether

Figure 15. Potential chloroethers from epichlorohydrin manufacture.

Initial inspection of the reaction mixture from the bis(1-chloromethyl-2-chloroethyl) ether synthesis number 5 (Section 6.2.1.5) by GC/MS indicated the major products were not the desired compound. GC/MS of step 1 of the crude reaction mixture from the epichlorohydrin synthesis (Section 6.2.2) indicated the presence of two major compounds with high boiling points. GC/MS of step 2 of the same synthesis showed the same two compounds. Neither of the mass spectra was identifiable by either manual or computer search routines. The earlier eluting of the two peaks gives a mass spectrum which is similar in some of its fragmentation patterns to the mass spectrum of bis(2-chloroallyl) ether. This mass spectrum, which to date defies interpretation, is shown for future reference in Figure 16. The spectrum of the later eluting compound is shown in Figure 17. It is possible through examination of fragmentation patterns, including chlorine isotope clusters, to assign the mass spectrum of this peak as either bis(1-chloromethyl,2-chloroethyl) ether or this compound plus the other two isomers shown in Figure 15. The mass fragment assignments for this mass spectrum are illustrated in Figure 18. Because of the limited amount of effort devoted to this study, no further purification or characterization of this compound was attempted. Water and air characterization samples from Freeport, Texas were, however, carefully examined for the presence of mass spectra matching Figure 17. No evidence of the presence of this spectrum was found in the GC/MS run of either sample.

6.2.1 Attempted Synthesis of bis(1-chloromethyl,2-chloroethyl) ether

Five experiments were performed in attempts to synthesize bis(1-chloromethyl-2-chloroethyl) ether. Each of the experimental procedures and results are briefly described in the following subsections.

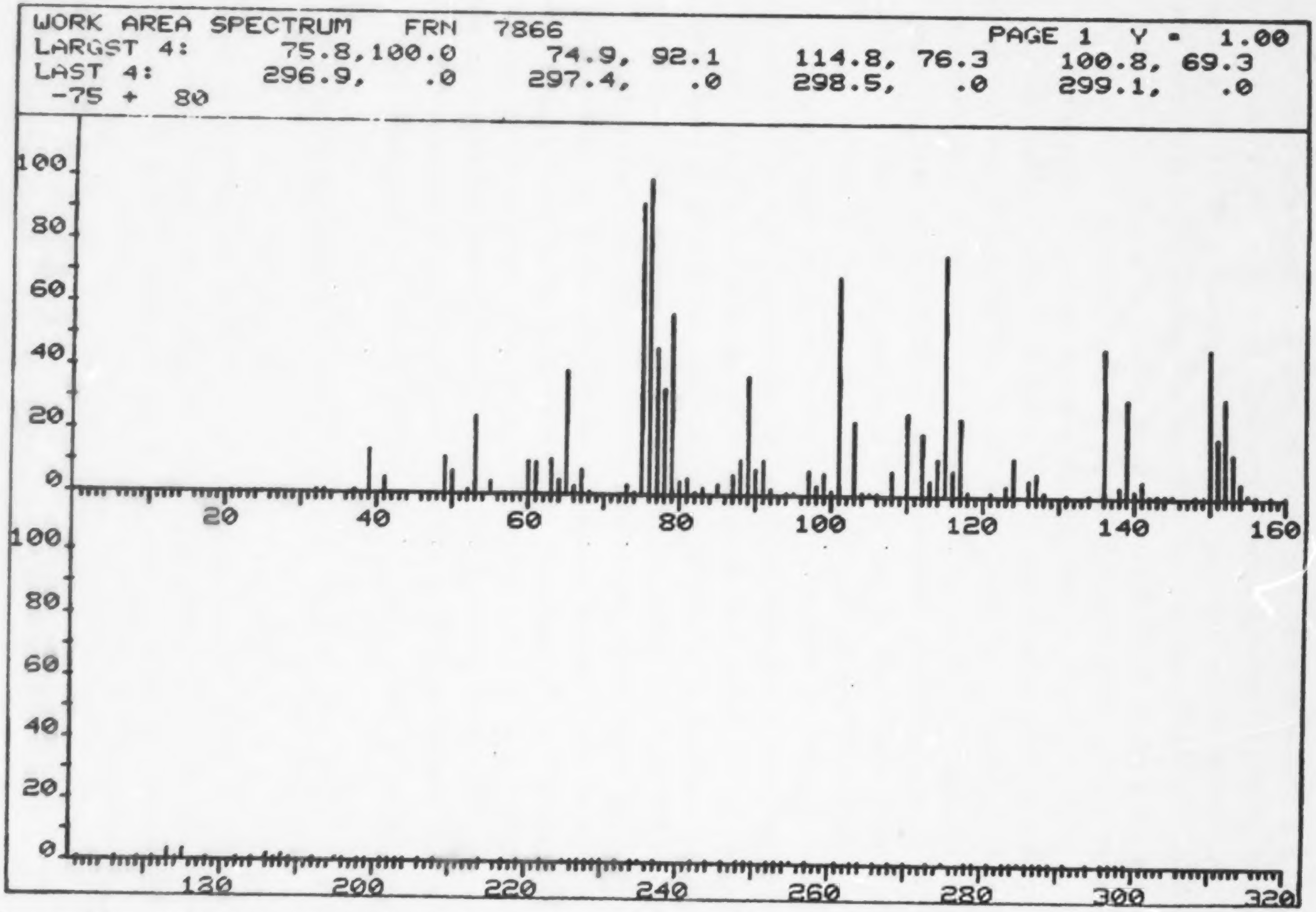
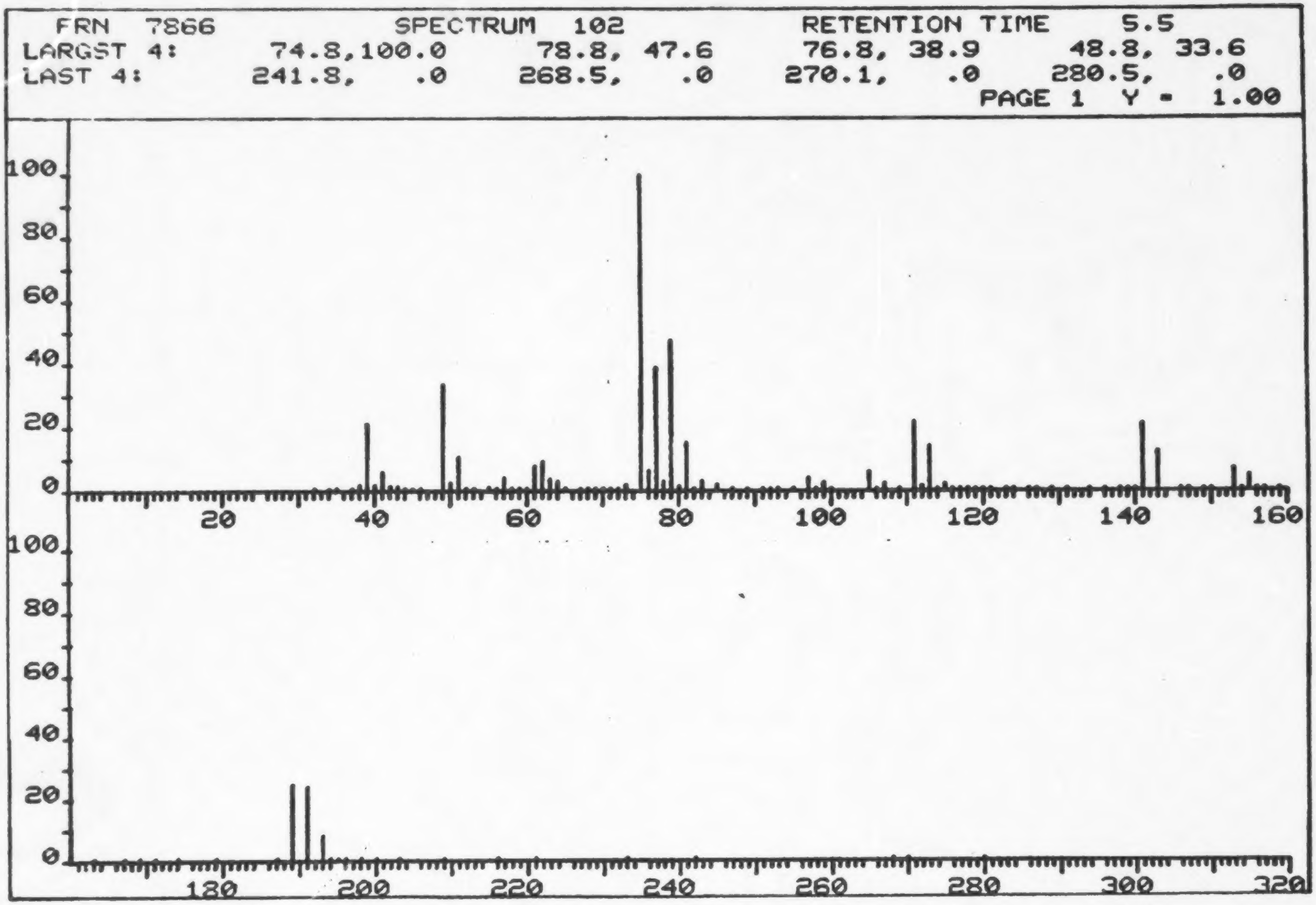


Figure 16. Mass spectrum of earlier eluting compound in epichlorohydrin synthesis mixture.



```
  FRN  7866            SPECTRUM  102              RETENTION TIME    5.5
LARGST 4:      74.8,100.0     78.8, 47.6     76.8, 38.9      48.8, 33.6
LAST 4:       241.8,    .0   268.5,    .0   270.1,    .0   280.5,    .0
                                                          PAGE 1  Y =  1.00
```

Figure 17. Mass spectrum of later eluting compound in epichlorohydrin synthesis mixture [bis(1-chloromethyl-2-chloroethyl)ether?].

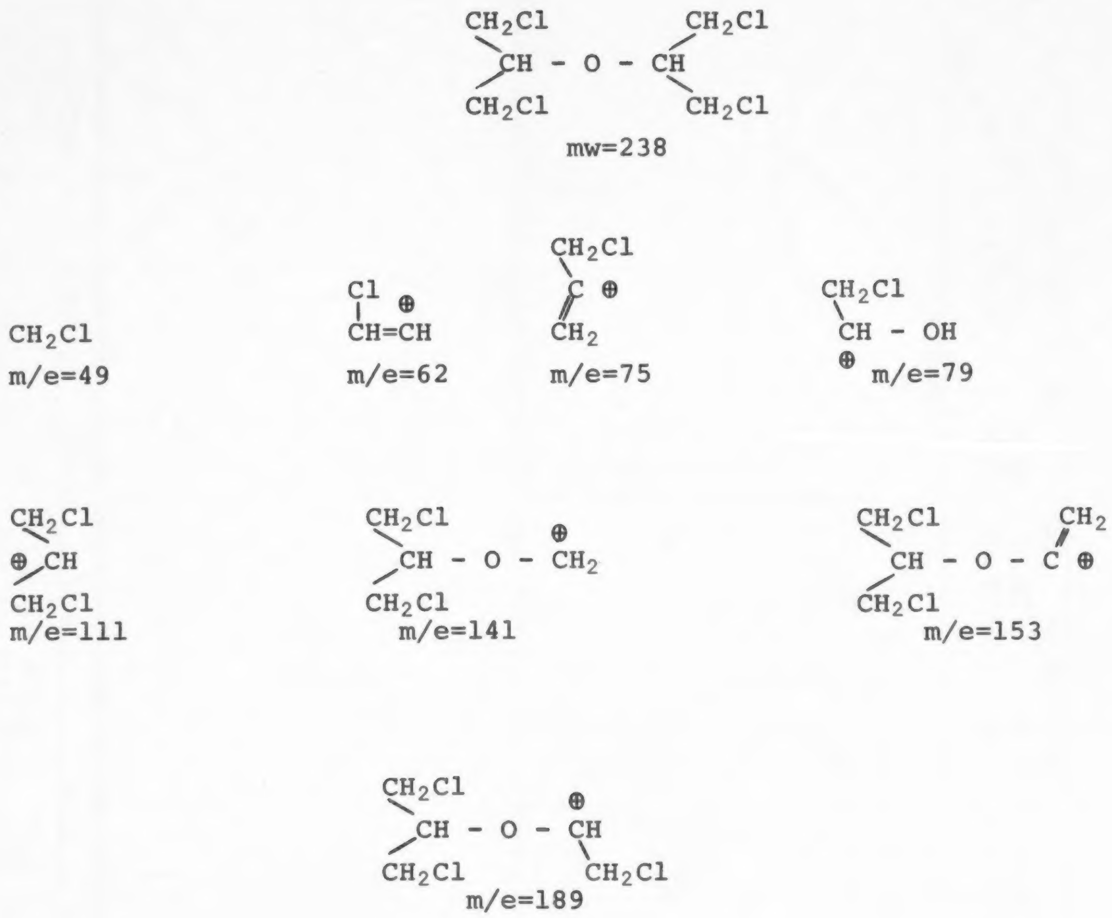
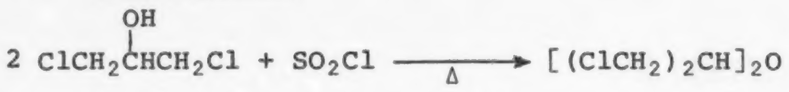

mw=238
m/e=49
m/e=62
m/e=75
m/e=79
m/e=111
m/e=141
m/e=153
m/e=189

Figure 18. Possible interpretation of mass fragments for BCMCEE (Figure 7).

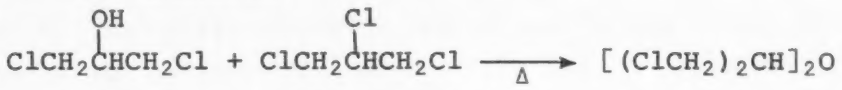
6.2.1.1 Experiment 1--



$$2\ \mathrm{ClCH_2\overset{OH}{C}HCH_2Cl} + \mathrm{SO_2Cl} \xrightarrow[\Delta]{} \mathrm{[(ClCH_2)_2CH]_2O}$$

Heating a mixture of 2 volumes of 1,3-dichloro-2-propanol and 1 volume of sulfuryl chloride overnight gave hydrogen chloride and a black tar.

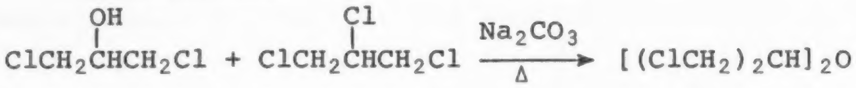
6.2.1.2 Experiment 2--



$$\mathrm{ClCH_2\overset{OH}{C}HCH_2Cl} + \mathrm{ClCH_2\overset{Cl}{C}HCH_2Cl} \xrightarrow[\Delta]{} \mathrm{[(ClCH_2)_2CH]_2O}$$

Heating equal volumes of 1,3-dichloro-2-propanol and 1,2,3-trichloropropane in a steam bath for 3 hours gave no hydrogen chloride. No change was discerned in the infrared spectrum of the mixture. Addition of triethylamine and warming gave rise to olefin absorption in the infrared but no indication of ether formation.

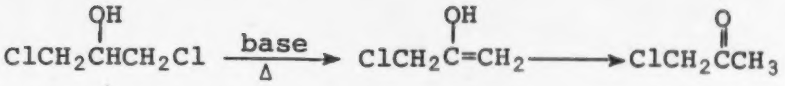
6.2.1.3 Experiment 3--



$$\mathrm{ClCH_2\overset{OH}{C}HCH_2Cl} + \mathrm{ClCH_2\overset{Cl}{C}HCH_2Cl} \xrightarrow[\Delta]{\mathrm{Na_2CO_3}} \mathrm{[(ClCH_2)_2CH]_2O}$$

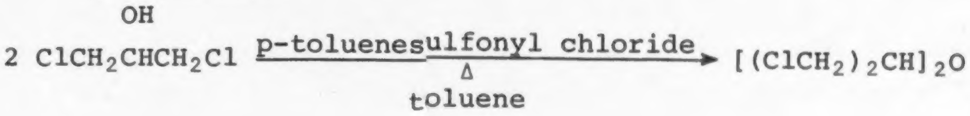
Equal volumes of 1,3-dichloro-2-propanol and 1,2,3-trichloropropane were stirred and heated to 115°C in the presence of anhydrous Na_2CO_3 for 3 hours with no reaction. The reaction mixture was then heated to 135°C for 19 hours. No reaction was detectable by infrared.

6.2.1.4 Experiment 4--
The addition of pyridine to a reaction mixture of the alcohol and trichlopropane and heating to 125°C gave a black, tarry material whose infrared spectrum showed olefin and carbonyl absorptions.



$$\mathrm{ClCH_2\overset{OH}{C}HCH_2Cl} \xrightarrow[\Delta]{\text{base}} \mathrm{ClCH_2\overset{OH}{C}{=}CH_2} \longrightarrow \mathrm{ClCH_2\overset{O}{\overset{\|}{C}}CH_3}$$

6.2.1.5 Experiment 5--



$$2\ \mathrm{ClCH_2\overset{OH}{C}HCH_2Cl} \xrightarrow[\substack{\Delta\\ \text{toluene}}]{\text{p-toluenesulfonyl chloride}} \mathrm{[(ClCH_2)_2CH]_2O}$$

Heating of 5 g of the alcohol with 0.5 g of p-toluenesulfonyl chloride in toluene at reflux overnight gave a mixture of alcohol and ether according to the infrared spectrum. A scale-up of the reaction to 43 g (0.33 moles) of alcohol gave one cm^3 of water in the attached Dean-Starke trap and water in the condenser. The solvent was changed to xylene and heating was continued under argon for 70 hours. The resultant tarry oil showed hydroxyl, ether and a trace of carbonyl absorption in its infrared spectrum.

6.2.2 Simulated Epichlorohydrin Synthesis

The synthesis shown in Section 6.2 was used to simulate the production of epichlorohydrin. The following conditions were employed for the synthesis. Chlorine gas [35.5 g (0.5 mole)] was bubbled slowly into a stirred mixture of 38.3 g (0.5 mole) of allyl chloride and 41 g of H_2O in a 250 cm^3 round-bottom, three-necked flask. The reaction of Cl_2 and H_2O results in the *in situ* generation of HOCl. HOCl then reacts with allyl chloride to form the chlorohydrin intermediates. The flask was equipped with a condenser and a bubbler atop the condenser to monitor the gas flow. The temperature rose to 73°C during this addition. A sample of this reaction mixture was analyzed by gas chromatography/mass spectrometry. The top aqueous phase of the reaction mixture was removed and a solution of 20 g

(0.5 moles) of NaOH in water was added to the cloudy oil that remained. The mixture turned yellow. This mixture was heated to 83-88°C for 2 hours. A sample of the cooled reaction mixture was analyzed by gas chromatography/mass spectrometry (see Section 6.2.1).

6.3 OTHER COMPOUNDS

At the request of EPA-OTS, a series of six compounds which could be formed along with the β-chloroethers were analyzed for in selected samples. The compounds are listed in Table 16 along with their boiling points and their three most intense mass spectral ions. The intensities of the mass ion are shown in parentheses. Each of the water and air characterization samples described in Section 6.4 were examined for these compounds. None of the six compounds were found in the air or water samples from the eight sites sampled.

TABLE 16. COMPOUNDS RELATED TO β-CHLOROETHERS

Compound	mw	Boiling Point, °C	1 m/e	2 m/e	3 m/e
2-chloroethanol	80	129	31(100)	27(8)	43(7)
1,3-dichloroacetone	126	173	77(100)	49(67)	79(32)
1,3-dichloro-2-propanol	128	174	79(100)	43(33)	81(32)
2,3-dichloro-2-propanol	128	182	62(100)	64(55)	31(26)
chloroacetic acid	94	189	50(100)	45(71)	41(64)
3-chloro-1,2-dihydroxypropane	110	213	44(100)	61(94)	43(89)

6.4 CHARACTERIZATION OF AIR AND WATER SAMPLES

A complete characterization of one air sample and one water sample from each of the last seven sites was performed by gas chromatography/mass spectrometry. Either an outfall or the #1 downstream water sample was reduced from the volume (2.5-3.5 cm^3) at which SIM analysis was performed to approximately 0.1 cm^3. 3 μl of this solution was then injected onto a 1.8 m x 2.1 mm glass column packed with 1% SP2250 on Supelcoport (100/120 mesh). The outlet of the column was connected to a Hewlett-Packard 5983 GC/MS. The column was programmed from 50°C to 260°C at 8°C/min. The mass spectrometer was scanned from 35 to 350 amu with a scan time of ∿ 4 sec. The sum of the ion responses during each scan were recorded as the total ion chromatogram. The mass spectra of peaks in the chromatogram were then examined. The mass spectra are then matched either manually or by computer matching programs.

The air samples were chosen from a point that should have a high concentration of materials being emitted from the plant. The Tenax GC tube was thermally desorbed using the apparatus shown in Figure 19. Helium was passed through the tube, which was heated in a modified tube furnace, in the opposite direction to the direction air was drawn through the tube during sampling. The components when desorbed were concentrated at the head of a 1.8 m x 2.1 mm glass column packed with Tenax GC (60/80 mesh) held at -30°C. The desorption temperature was 250°C. The tubes were desorbed for 5 minutes and then the chromatographic column was programmed at 30°C/min for 2.67 min then at 10°C/min to 230°C. The mass spectra were recorded under the mass spectral conditions listed for the water samples. The mass spectra of the peaks were again matched to listed mass spectra. (Results for each of the water and air sample characterizations are listed in Sections 8-15).

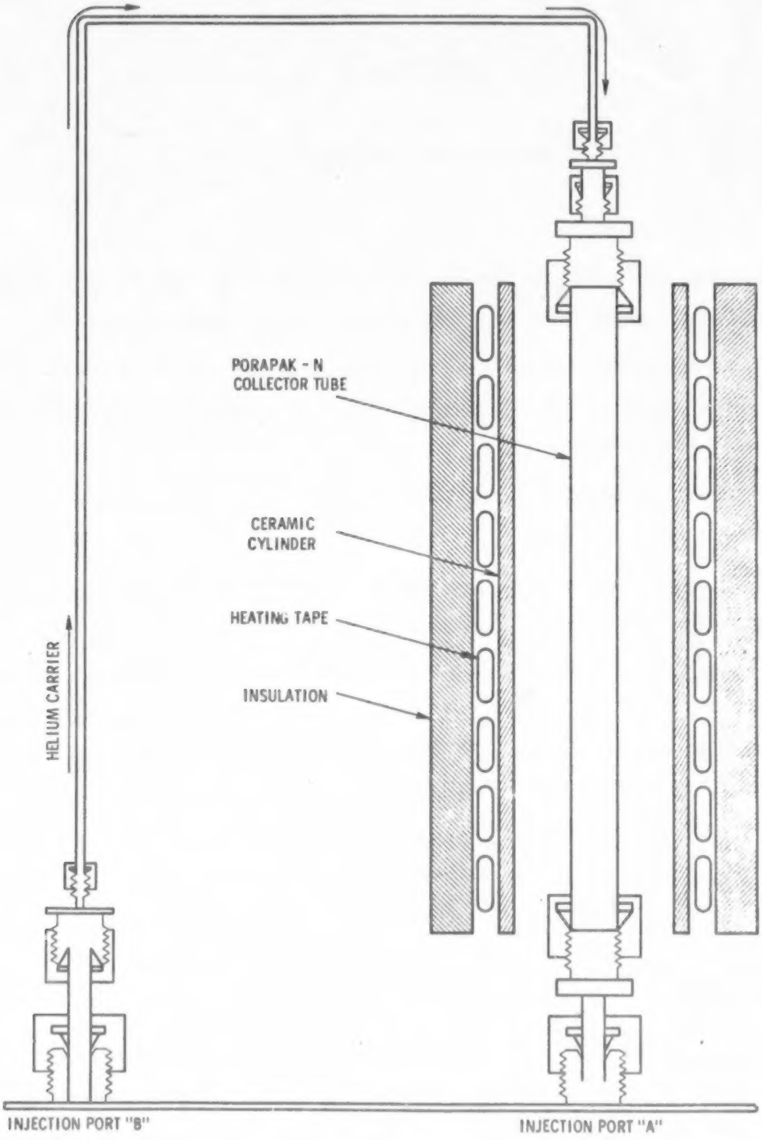

PORAPAK - N
COLLECTOR TUBE
CERAMIC
CYLINDER
HEATING TAPE
INSULATION
HELIUM CARRIER
INJECTION PORT "B"
INJECTION PORT "A"

Figure 19. Thermal desorption apparatus.

SECTION 7

RECOVERY STUDIES

The efficiency of the methods described in Sections 5 and 6 for recovery of six β-chloroethers from air, water and soil samples was determined under laboratory and field conditions. The procedures and results of these studies are described in the following subsections.

7.1 LABORATORY RECOVERY STUDIES

Recovery studies were conducted in the laboratory using β-chloroether standards. These tests were performed to determine the relative efficiency of the methods which were to be used for field samples. Matrices similar to those for field samples of air, water and soil were spiked with known amounts of β-chloroethers. These spiked samples were then subjected to the methods which were used for field samples.

7.1.1 Air

A number of tests were conducted using Tenax tubes spiked with β-chloroethers. First, 100 μl of a β-chloroether standard containing $\sim 2.5 \times 10^{-4}$ g/cm^3 of each of the ethers was injected onto the end of a Tenax-GC tube. The tube was then solvent desorbed with methanol using the desorption apparatus shown in Figure 7 at a rate of 0.5 cm^3/min. One-milliliter fractions were collected. The fractions were then analyzed on a Tenax-GC column using a flame ionization detector. Results are listed in Table 17. These results show the applicability of the solvent desorption method for recovery of β-chloroethers. Then to test the best method for conditioning the Tenax-GC tubes, two tubes were spiked with 100 μl of methylene chloride containing ∿2.5 x 10^{-4} g/cm^3 of each of the β-chloroethers. Tube A was conditioned by rinsing with 100 ml of methanol and then heating to 100°C for one hour under a flow of nitrogen. Tube B was conditioned for 16 hours at 300°C with a flow of nitrogen. After spiking, both tubes were subjected to an air flow rate of 1 liter/minute for 4 hours. Charcoal tubes were placed in front and behind the tubes. The charcoal in front was to remove materials from the laboratory air. The tube in back was to catch any β-chloroethers passing through the Tenax-GC. Results for these tubes, again in 1 cm^3 increments, are listed in Table 18. Since the results were very similar, the consistency of the thermally conditioned tube resulted in this being the method of choice for conditioning. Two other tubes were spiked with 100 μl and 200 μl respectively of the ∿2.5 x 10^{-4} g/cm^3 of each β-chloroether standard solution. Air was then drawn through these tubes for 6 hours at 1 liter/minute. The total percentage recovery for each tube is shown in Table 19. Again, the tubes showed a similar distribution percentage as was seen for the thermally conditioned tube described in Table 18 for the 1 cm^3 increments.

The results for the 100 μl standard may have included contaminants from lab air since a charcoal tube was not used in front of this Tenax-GC tube. Average recovery for the tube B described in Table 18 and the two tubes in Table 16 were CEVE/CEEE-90%, BCEE-97% (excluding the 158% value), BCIPE-96%, BCEXM-97%, and BCEXE-85%. These data show that the efficiency of the desorption technique is more than adequate for this study. A final experiment was performed to determine whether the volume of methanol could be reduced from 4 ml to 0.4 ml after desorption using a micro-Snyder column. The percentage recoveries were

TABLE 17. RECOVERY OF β-CHLOROETHERS FROM TENAX-GC. 100 μl OF ~2.5 x 10^{-4} g/cm³ OF EACH β-CHLOROETHER ADDED

	% Recovery				
cm³	CEVE/CEEE	BCEE	BCIPE	BCEXM	BCEXE
0-1	68	75	67	71	67
1-2	14	18	16	11	15
2-3					
3-4					
Total	82	93	83	82	82

TABLE 18. RECOVERY OF β-CHLOROETHERS FROM TENAX-GC - EFFECTS OF CONDITIONING

Tube A - Solvent Conditioned

cm^3	CEVE/CEEE	BCEE	BCIPE	BCEXM	BCEXE
0-1	24	51	43	40	35
1-2	26	35	27	44	32
2-3	15	15	12	14	13
3-4	5	-	-	-	-
Total	69	101	82	98	80

Tube B - Thermally Conditioned

cm^3	CEVE/CEEE	BCEE	BCIPE	BCEXM	BCEXE
0-1	48	71	64	66	54
1-2	25	18	20	26	16
2-3	8	-			
3-4	3	-			
Total	85	89	84	92	70

TABLE 19. RECOVERY OF β-CHLOROEHERS FROM TENAX-GC - EFFECTS OF AIR PULLED THROUGH TUBES FOR 6 HOURS

	% Recovery				
	CEVE/CEEE	BCEE	BCIPE	BCEXM	BCEXE
100 µl of 2.5 x 10^{-4} g/cm^3 std.	87	158	112	105	97
200 µl of 2.5 x 10^{-4} g/cm^3 std.	98	106	91	94	88

CEVE/CEEE-9%, BCEE-49%, BCIPE-44%, BCEXM-43% and BCEXE-38%. These results indicated that it would be best not to use the micro-Snyder system without further study.

7.1.2 Water

A series of 1 liter samples of deionized water were spiked with 50, 100 and 200 μl of a standard containing 2.5×10^{-4} g/cm^3 of each of the β-chloroethers. These solutions were then extracted three times with 100 ml portions of methylene chloride. The methylene chloride extracts were combined and evaporated to a volume of ∿2 cm^3 in a Kuderna-Danish evaporator. The concentrates and rinses were transferred to a septum caped vial and analyzed on a Tenax-GC column with a flame ionization detector. The results of these recovery studies are listed in Table 20. The upper half of the table lists the percent recovery for each of the spiked samples and the average recovery for the four samples. These recovery data indicate the extraction and concentration techniques are more than adequate for this study. The lower half of the table lists the resultant concentration of each β-chloroether in the water after spiking. Earlier experiments with reducing the volume of the concentrates to ∿0.4 cm^3 with the micro-Snyder column had shown ∿40-50% recovery of the spiked samples.

7.1.3 Soil

A series of 50 g samples of soil were Soxhlet extracted twice for 16 hours with methylene chloride. These soil samples were then spiked with 25, 50, 100 and 200 μl of a standard containing ∿2.5×10^{-4} g/cm^3 of each of the β-chloroethers. The spiked samples were then ~~re-~~extracted for 16 hours with methylene chloride in a Soxhlet extractor. The extracts were combined and concentrated to ∿2 cm^3 in a Kuderna-Danish evaporator. The concentrate and rinses were combined and analyzed on a Tenax-GC

TABLE 20. RECOVERY OF β-CHLOROETHERS FROM WATER

		% Recovery				
		CEVE/CEEE	BCEE	BCIPE	BCEXM	BCEXE
50 μl		34.8	75.0	71.7	72.4	70.3
100 μl		76.9	91.0	87.6	87.5	91.8
100 μl		72.0	90.7	89.7	89.9	92.0
200 μl		81.2	100.3	97.7	99.8	105.0
	Average	66.2	89.3	86.7	87.4	89.8

	microgram/l				
	CEVE/CEEE	BCEE	BCIPE	BCEXM	BCEXE
50 μl	21.2	12.7	11.5	12.5	12.8
100 μl	42.4	25.4	23.0	25.0	25.6
200 μl	84.8	50.8	46.0	50.0	51.2

column with a flame ionization detector. The results of these recovery studies are listed in Table 21. The upper half of the table is the percent recovery for each compound for a given spike and the lower half is the resultant concentration of each β-chloroether in the soil after spiking. The average for the five samples is included at the end of the upper half of the table. These average recovery data indicate that while recovery is not optimum it is sufficient for this study. The value of 177.9% for the BCEE 50 μl spike is excluded from the average calculation. This value is assumed to be due to an interfering compound which elutes at a retention time similar to the retention time of BCEE. Since a flame ionization detector was used for this study, specific detection was not possible.

7.2 FIELD RECOVERY STUDIES

Studies were conducted to determine the effects of transportation and storage as well as the extraction, concentration and analysis steps on samples taken in the field.

7.2.1 Air

A blank Tenax tube was spiked with a mixture of the six β-chloroethers in methanol at each of four field sites. The Swagelok cap was removed from one end of the tube and 100 μl of the mixture containing $\sim 2.5 \times 10^{-4}$ g/cm^3 of each of the β-chloroethers was injected onto the Tenax resin. The tube was then recapped and treated in the same manner as sample tubes with regard to shipment and storage. Each tube was then solvent desorbed with 4 ml at the same time that tubes from that site were desorbed. The desorption was performed using the apparatus shown in Figure 7. Methanol was collected in 5 cm^3 capacity vials with screw caps. The center of the screw caps was open and closure was achieved with a Viton spetrum. The solutions from this spiked tube were then analyzed by GC/MS/SIM at the

TABLE 21. RECOVERY OF β-CHOROETHERS FROM SOIL

µl added	% Recovery				
	CEVE/CEEE	BCEE	BCIPE	BCEXM	BCEXE
25	-	58.4	87.9	57.7	76.2
50	31	179.9	96.6	64.8	77.6
100	25	56.1	59.9	59.4	70.9
100	30	50.8	53.3	53.1	65.7
200	25.4	53.0	55.5	51.1	59.5
Average	27.9	54.6	70.6	57.2	70.0

µl added	µg/gram of soil				
	CEVE/CEEE	BCEE	BCIPE	BCEXM	BCEXE
25	0.212	0.127	0.115	0.125	0.128
50	0.414	0.254	0.230	0.250	0.256
100	0.828	0.508	0.460	0.500	0.512
200	1.656	1.016	0.920	1.000	1.024

same time as the samples from each site were analyzed. The results for each of the β-chloroethers from the four sites and the average for the four are shown in Table 22. The average recovery for the four field samples was 74.8% as compared with 93% for the laboratory studies. These results indicate an average loss of 18.2% during transport and storage of the air samples.

7.2.2 Water

Two extra water samples (approximately 1 liter volume) were collected at six of the sampling sites at the upstream water sample location. One sample from each site was spiked with the mixture of β-chloroethers. The other sample was used as a control. The concentration of each of the β-chloroethers in the spiking solution was $\sim 2.5 \times 10^{-4}$ g/cm^3. 100 μl of the spiking solution was added in the field immediately after sampling to each of the six water samples. These water samples were then transported, extracted, concentrated and analyzed along with the water samples from each site. The samples were in transit and storage approximately 7 to 10 days before extraction and concentration. The samples were extracted three times with 100 ml portions of methylene chloride. The combined methylene chloride extracts were then concentrated to a volume of ~ 2 cm^3 in a Kuderna-Danish evaporator. The concentrates and rinses were transferred to a septum capped vial and analyzed by GC/MS/SIM. Results for the field spiked water samples are shown in Table 23. The average percent recovery for the six β-chloroethers from field doped samples was 77.3% compared with 83.9% recovery for the laboratory studies. This 6.6% decrease in recovery reflects the losses due to transportation, storage, and biological action of the water samples.

TABLE 22. FIELD RECOVERY STUDIES - AIR

Compound	Spike, µg	Freeport, TX Amount measured, µg	Freeport, TX Percent recovered	Port Neches, TX Amount measured, µg	Port Neches, TX Percent recovered	Plaquemine, LA Amount measured, µg	Plaquemine, LA Percent recovered	Moss Point, MS Amount measured, µg	Moss Point, MS Percent recovered	Average Amount measured, µg	Average Percent recovered
CEEE	20.6	24.4	118.5	18.6	90.4	17.3	83.8	15.9	77.1	19.0	92.5
CEVE	21.9	11.4	52.2	7.1	32.4	16.2	73.9	13.9	63.5	12.2	55.5
BCEE	25.4	18.2	71.8	11.8	46.6	23.3	92.1	21.1	82.9	18.6	73.2
BCIPE	22.9	18.6	81.1	14.2	61.9	23.2	101.0	21.6	94.4	19.4	84.7
BCEXM	25.0	14.8	59.3	7.1	28.4	23.4	93.3	22.4	89.6	16.9	67.7
BCEXE	25.5	15.4	60.6	6.1	24.0	29.2	114.6	26.1	102.2	19.2	75.3

TABLE 23. FIELD RECOVERY STUDIES - WATER

Compound	Spike, µg	Percent recovered						
		Freeport, TX	Port Neches, TX	Plaquemine, LA	Moss Point, MS	Institute, WV	Rochester, NY	Average
CEEE	20.6	113.1	86.9	86.7	77.0	42.2	29.6	72.6
CEVE	21.9	92.7	50.2	61.5	48.7	50.7	41.5	57.6
BCEE	25.4	118.5	78.0	76.4	72.3	64.6	70.1	80.0
BCIPE	22.9	116.6	113.1	50.3	100.3	61.1	67.6	84.8
BCEXM	25.0	113.2	79.3	77.0	72.7	66.4	69.6	79.7
BXEXE	25.5	117.3	98.8	91.1	86.3	73.7	68.6	89.3

7.2.3 Soil

One soil sample taken at Freeport, Texas was spiked in the field with 100 μl of the β-chloroether mixture. The concentration of the six β-chloroethers in the spiking solution was ∿2.5 x 10^{-4} gm/cm^3. The sample was then sealed in the canning jar and transported back to Dayton. The entire soil sample (∿365 g) was then extracted in a large Soxhlet extractor. The methylene chloride solution used for the extraction was concentrated in a Kuderna-Danish evaporator to a volume of ∿ 2 cm^3. This concentrate and rinses were then transferred to a septum capped vial and analyzed by GC/MS/SIM. The recoveries for this sample were CEE - 34%, CEVE - 0%, BCEE - 46.5%, BCIPE - 0%, BCEXM - 36.8% and BCEXE - 41.6%. The nonrecovery of CEVE is not surprising in view of the hydrolytic instability of the compound particularly toward acid conditions; however, the reason for the nonrecovery of BCIPE from this sample is unknown.

7.3 ASSESSMENT OF ERROR

7.3.1 Sample Collection

Two sources of error in the collection of air samples are: (1) the collection efficiency of the Tenax-GC tubes and (2) the error in measuring the volume of air passed through the tube. The collection efficiency of Tenax-GC for BCEE has been reported to be virtually 100% (59). The error associated with the measurement of the total volume of air passing through the Tenax tube is estimated to be ±10%.

For water samples, the source of error in sample collection is the measurement of the volume of water taken for extraction. This error is estimated to be ±2.0%.

7.3.2 Sample Workup and Analysis

7.3.2.1 Air--

An estimate of the combined error associated with the workup and analysis of air samples may be determined from the data concerning the recovery of field-spiked samples. These data were discussed in detail in Section 7.2.1. Table 24 lists the average percent recovered for the six β-chloroethers, the standard deviation for spiked samples from four sites, and the percent relative standard deviation (RSD) for each compound. The average percent RSD for the six compounds was ±33.1% and represents the average error for sample workup and analysis of air samples. This potential deviation includes errors associated with measurement of volume of dopant solution added to the tubes, solvent desorption, GC/MS analysis, final volume measurement and volumetric, dilution, and pipetting errors.

7.3.2.2 Water--

In a manner similar to that just described for air samples, the data related to the recovery of spiked field water samples can be used to calculate an estimate of error occuring during sample workup and analysis of water samples for β-chloroethers. The recovery of field-spiked water samples and results are described in Section 7.2.2 Table 25 lists the average percent recovery for the six β-chloroethers from spiked water samples, and standard deviation and percent RSD for each compound. The average percent RSD for the six compounds was ±29%. This value represents an estimate of the average error possible during sample workup and analysis of water samples. Contributing sources of error for the β-chloroether water samples include the reproducibility of extraction Kuderna-Danish evaporation, GC/MS analysis, addition of doping solution and in determination of the final sample volume. Also included are the effects of biological and chemical action on the β-chloroethers in the water samples during transport and storage.

TABLE 24. ASSESSMENT OF ERROR IN β-CHLOROETHER AIR SAMPLE WORKUP AND ANALYSIS.

β-Chloroether	Average Recovered, %	Standard Deviation	RSD, %
CEEE	92.5	18.2	19.7
CEVE	55.5	17.8	32.1
BCEE	73.2	19.7	26.9
BCIPE	84.7	17.2	20.3
BCEXM	67.7	30.3	44.8
BCEXE	75.3	41.3	54.8
		Average RSD =	±33.1

TABLE 25. ASSESSMENT OF ERROR IN β-CHLOROETHER WATER SAMPLE WORKUP AND ANALYSIS.

β-Chloroether	Average Recovered, %	Standard Deviation	RSD, %
CEEE	72.6	31.1	42.8
CEVE	57.6	18.4	31.9
BCEE	80.0	19.5	24.4
BCIPE	84.8	28.6	33.7
BCEXM	79.7	17.1	21.5
BCEXE	89.3	17.7	19.8
		Average RSD =	±29.0

7.3.2.3 Soil and Sediment--

An estimate of error associated with sample workup of soil and sediment β-chloroether samples can be determined from the average percent RSD for doped laboratory soil samples. The data listed in Table 26 were compiled from Section 7.1.2. The table includes the average percent recovered for each of the six β-chloroethers, and standard deviation and percent RSD for each ether. The average percent RSD for the six compounds is ±12.7%.

Since these data were generated with a flame ionization detector, an estimate of error associated with GC/MS analysis was needed. This estimate can be made from data related to the reproducibility of standard injections. These data are shown in Table 27. The average percent RSD for the six β-chloroethers is ±8.3%. Errors contributing to the estimated errors for β-chloroether soil and sediment sample workup and analysis are related to the reproducibility of Soxhlet extraction, Kuderna-Danish evaporation, and GC/MS analysis. Also, errors in final volume measurement and addition of standard to the soil contribute to the overall error.

7.3.3 Total Error

An estimate of the total error can be obtained by summing the squares of the individual sources of error and the extracting the square root of this sum. Implicit in this estimation is the assumption that the individual sources of error are independent. The total estimated error for air, water, and soil/ sediment samples is listed in Table 28.

TABLE 26. ASSESSMENT OF ERROR IN β-CHLOROETHER SOIL AND SEDIMENT WORKUP.

β-Chloroether	Average Recovered,%	Standard Deviation	±RSD,%
CEEE/CEVE	27.9	2.7	9.7
BCEE	54.6	2.9	5.3
BCIPE	70.6	20.1	28.5
BCEXM	57.2	5.4	9.4
BCEXE	70.0	7.5	10.7

Average RSD = ±12.7

TABLE 27. REPODUCIBILITY OF GC/MS ANALYSIS FOR β-CHLOROETHERS. REPLICATE INJECTIONS OF A STANDARD β-CHLOROETHER MIX ON JULY 26, 1977.

Inj.	CEEE Area	CEVE Area	BCEE Area	BCIPE Area	BCEXM Area	BCEXE Area
1	152659	79072	368941	288120	362343	296448
2	141018	73969	345212	266176	348405	258510
3	116401	63463	325876	237612	325447	236424
4	147918	74276	364755	284882	362097	283743
Mean	139499	72695	351196	269198	349573	268781
S.D.	16123	6583	19796	23172	17353	26719
%RSD	11.6	9.1	5.6	8.6	5.0	9.9

Average RSD = ±8.3%

TABLE 28. TOTAL ESTIMATED ERROR

Sample Matrix	Total Error, %
Air	±34.6
Water	±29.0
Soil/Sediment	±15.2

SECTION 8

SAMPLING AND ANALYSIS FOR β-CHLOROETHERS AT OLIN CORPORATION, BRANDENBURG, KENTUCKY

8.1 PRESAMPLING SURVEY

8.1.1 Description of the Plant Site

Olin Corporation is located on Doe Run Road east of Brandenburg, Kentucky. The mailing address of the plant is Box 547, Brandenburg, Kentucky, 40108. The plant produces a variety of industrial organic chemicals. Among the chemicals reported to be produced at this plant are ethylene oxide and propylene oxide. Production capacity for propylene oxide which is produced via the chlorohydrin route is 6.0×10^7 kg/yr. Production capacity for ethylene oxide production which is reported to be produced via direct oxidation is 5.1×10^7 kg/yr. A by-product of propylene oxide production by the chlorohydrin route is bis(2-chloroisopropyl) ether.

A presurvey of the plant area was performed on 30 April 1977. The presurvey consisted of visual inspection of the Olin complex, since contact with plant personnel was not allowed, and selection of sites for air and water sampling.

The Olin complex site consists of a large number of buildings including a power plant, open construction facilities, distillation and cooling towers, storage tanks for liquids and gases and settling ponds. The wastewater from the plant enters Doe Run and after traveling a short distance ($\sim$ 1 km) enters the Ohio River.

The location of the plant is shown on the topographical map of the area in Figure 20. The plant encompasses an area of 1 km east to west along Doe Run Road on the south bank of the Ohio River and 0.8 km north to south from the Ohio River to Doe Run Road. The overall distance east to west of property owned by Olin is ∿ 3.6 km. A panoramic photograph of the plant taken from the north bank of the Ohio River is shown in Figure 21. The plant is bounded on the north by the Ohio River, to the east by Doe Run Creek, to the south by Doe Run Road and a series of foothills and to the west by the small town of Brandenburg, Ky. Brandenburg is 4.2 km west of the plant.

8.1.2 Surrounding Area

The Brandenburg area is located in northwest Kentucky about 80 km west of Louisville. The plant site is located in Meade County, Kentucky. Elevation of the area ranges from 114 m at the Ohio River to 204 m at the tops of some of the foothills. The plant site is situated on a flat plain of the Ohio River. Brandenburg is the only concentration of population in the area of the plant. The population of Brandenburg, Ky. is 1637.

No other industry is located in the area of the Olin plant. Vegetation in the area consists of a variety of types of deciduous trees. The only visible emissions from the plant during presurvey and sampling were steam vents and the power plant. No odor was detected in the vicinity of the plant.

8.2 SAMPLING AND ANALYSIS RESULTS

Sampling of the area around Olin Corporation, Brandenburg, Kentucky for β-chloroethers was conducted on 30 March - 1 April 1977. The conditions, locations and results for air, water and soil samples collected during this sampling trip are discussed in the following subsections.

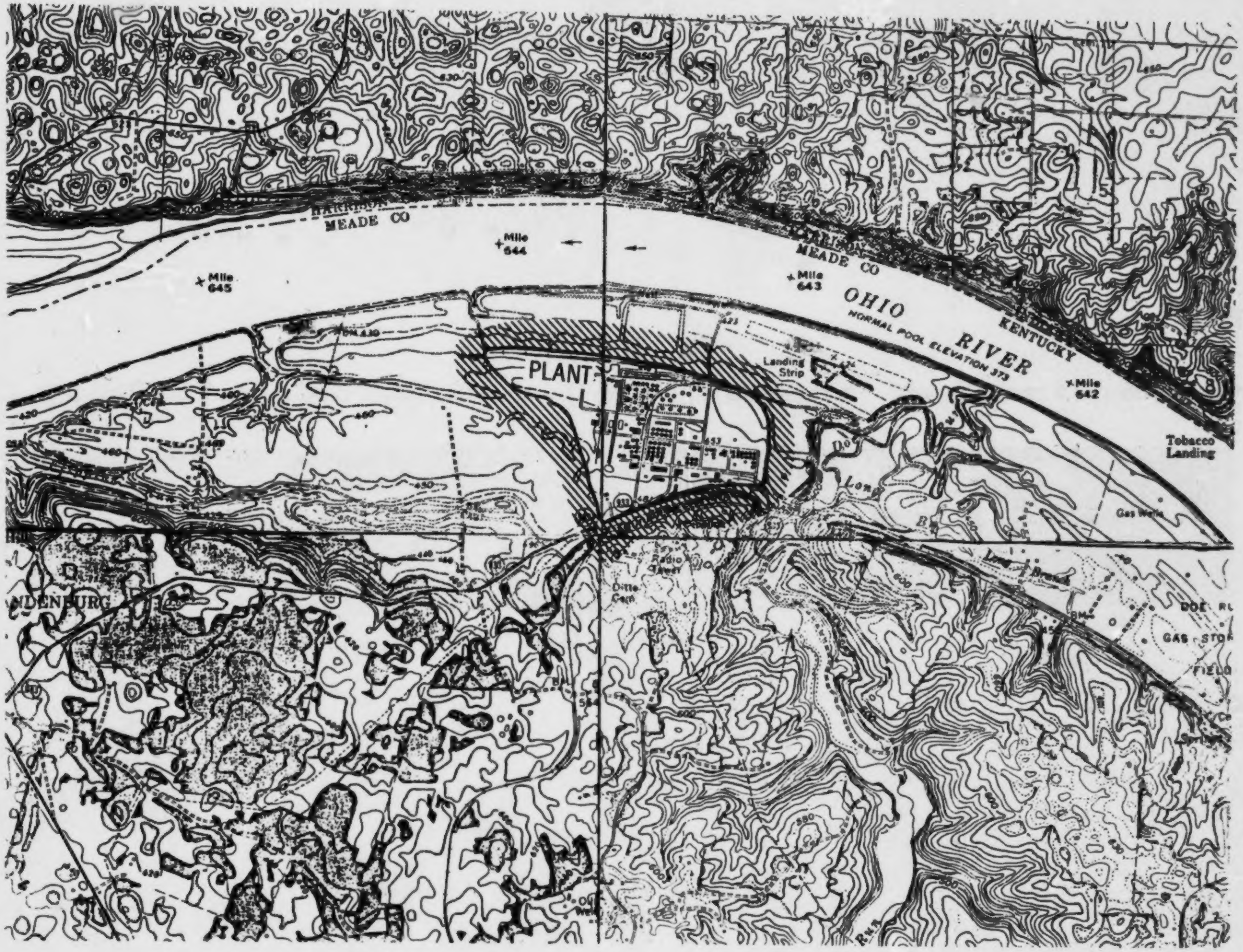

MEADE CO
Mile 645
Mile 644
Mile 643
Mile 642
MEADE CO
OHIO RIVER
NORMAL POOL ELEVATION 373
KENTUCKY
PLANT
Landing Strip
Tobacco Landing
Gas Wells
Long Branch
Radio Tower
Ditto Cem
NDENBURG

Figure 20. Approximate plant boundaries at Olin Corporation, Brandenburg, Kentucky.

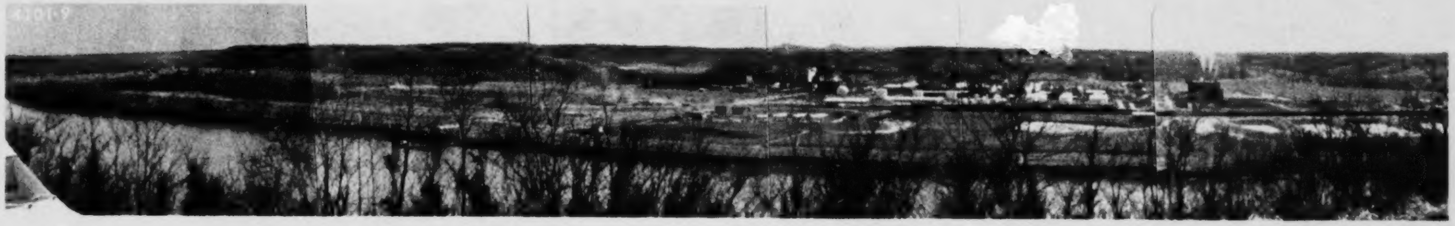


Figure 21. Composite panoramic photograph of Olin Corporation, Brandenburg, Kentucky.

8.2.1 Air Samples

Air sampling around Olin, Brandenburg, Ky. was conducted in two ways. A sampling array was set up as shown in Figure 22. A series of perimeter samples was also collected. The locations of the array samples are shown on the topographical map of the area in Figure 23. The location of the perimeter samples on the same map is shown in Figure 24. The sample numbers, location, compass reading relative to the center of the plant, sampling start, stop times, duration and volume are shown in Table 29. Wind speed and direction data are recorded in Table 30. The sampling was accomplished with stainless tables 20 cm long x 0.45 cm inside diameter packed with Tenax GC. The sampling was performed with rotary vane pumps of the type used for EPA method 5 stack sampling. This pump required propane-fueled electrical generators. Because of the large pressure drop through these 0.45 cm inside diameter tubes, even with these large pumps, a sufficient flow rate was not achieved.

The tubes were analyzed by methanol desorption (1 cm^3) followed by GC/MS/SIM on a HP5982 GC/MS. None of the six β-chloroethers of interest were found in the samples. Average detection limit for the array samples was 9.3×10^{-6} g/m^3 and average detection limit for the perimeter samples was 6.3×10^{-6} g/m^3. These results led to the improvements in the sampling and analysis methods described in Section 4 and 6 of the report.

8.2.2 Water Samples

An upstream, an outfall and two downstream water samples were collected during 30-31 March 1977 from Doe Run Creek near Olin Corporation, Brandenburg, Ky. The samples at the upstream and downstream locations were collected with tool box samplers described in Section 4. The outfall sample was collected with an ISCO compositing sampler. Location of the samples is shown in

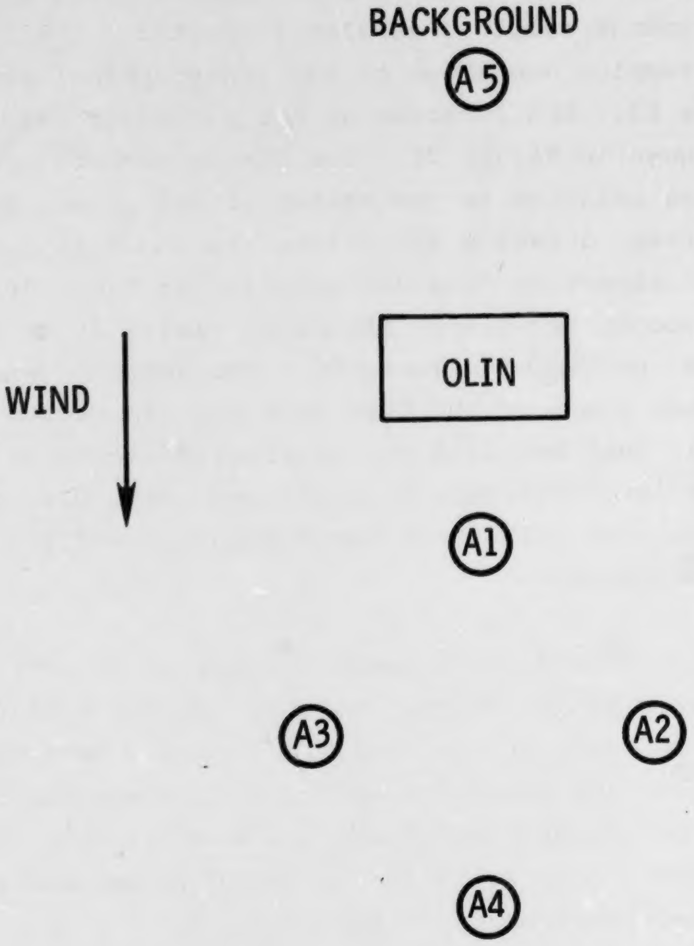

BACKGROUND
A5
OLIN
WIND
A1
A3
A2
A4

Figure 22. Diagram of array air samplers at Olin Corporation, Brandenburg, Ky.

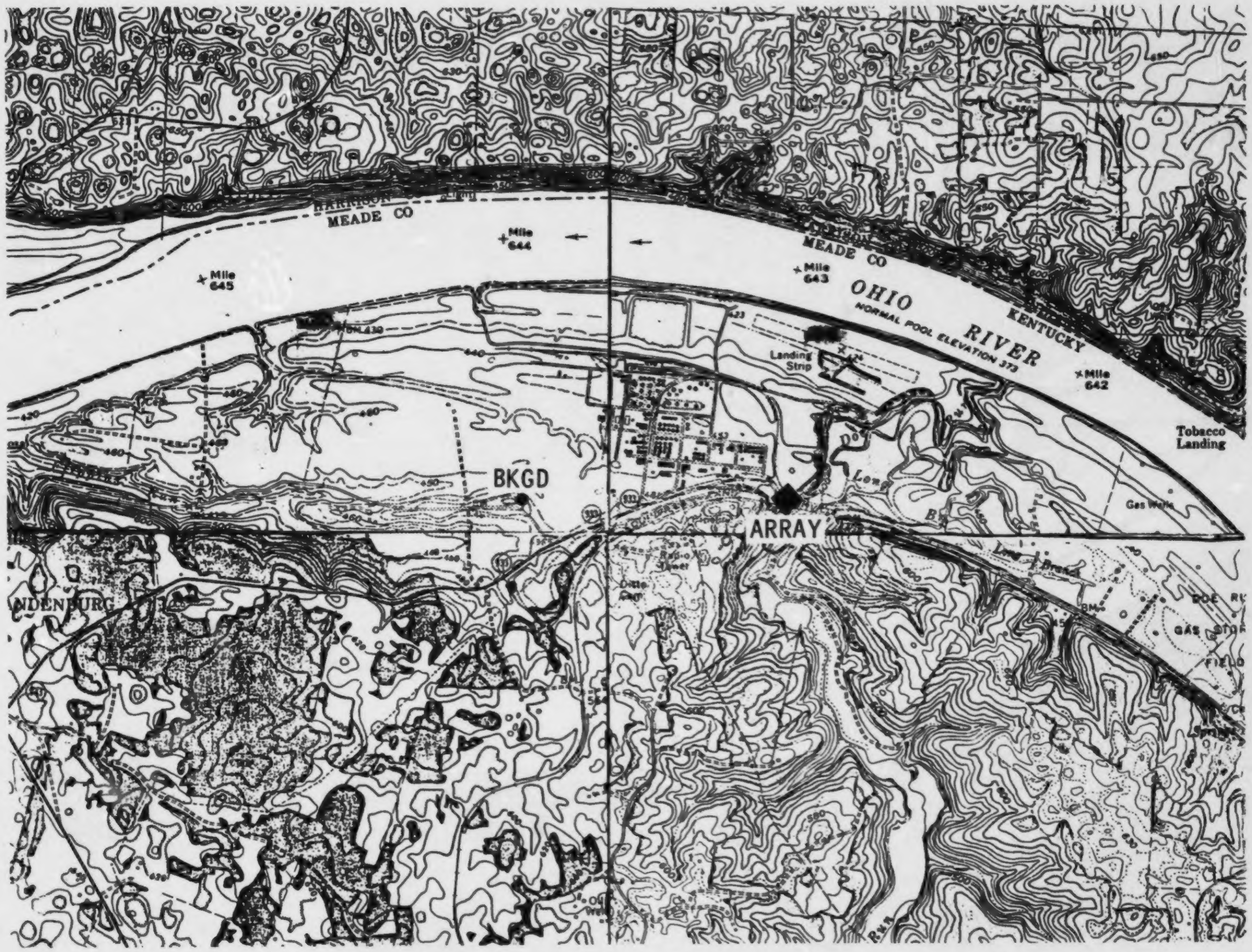

OHIO RIVER
NORMAL POOL ELEVATION 373
KENTUCKY
MEADE CO
MEADE CO
HARRISON
Mile 642
Mile 643
Mile 644
Mile 645
Tobacco Landing
Landing Strip
Gas Wells
BKGD
ARRAY
Long Branch
BRANDENBURG

Figure 23. Air sampling sites-array at Olin Corporation, Brandenburg, Ky.

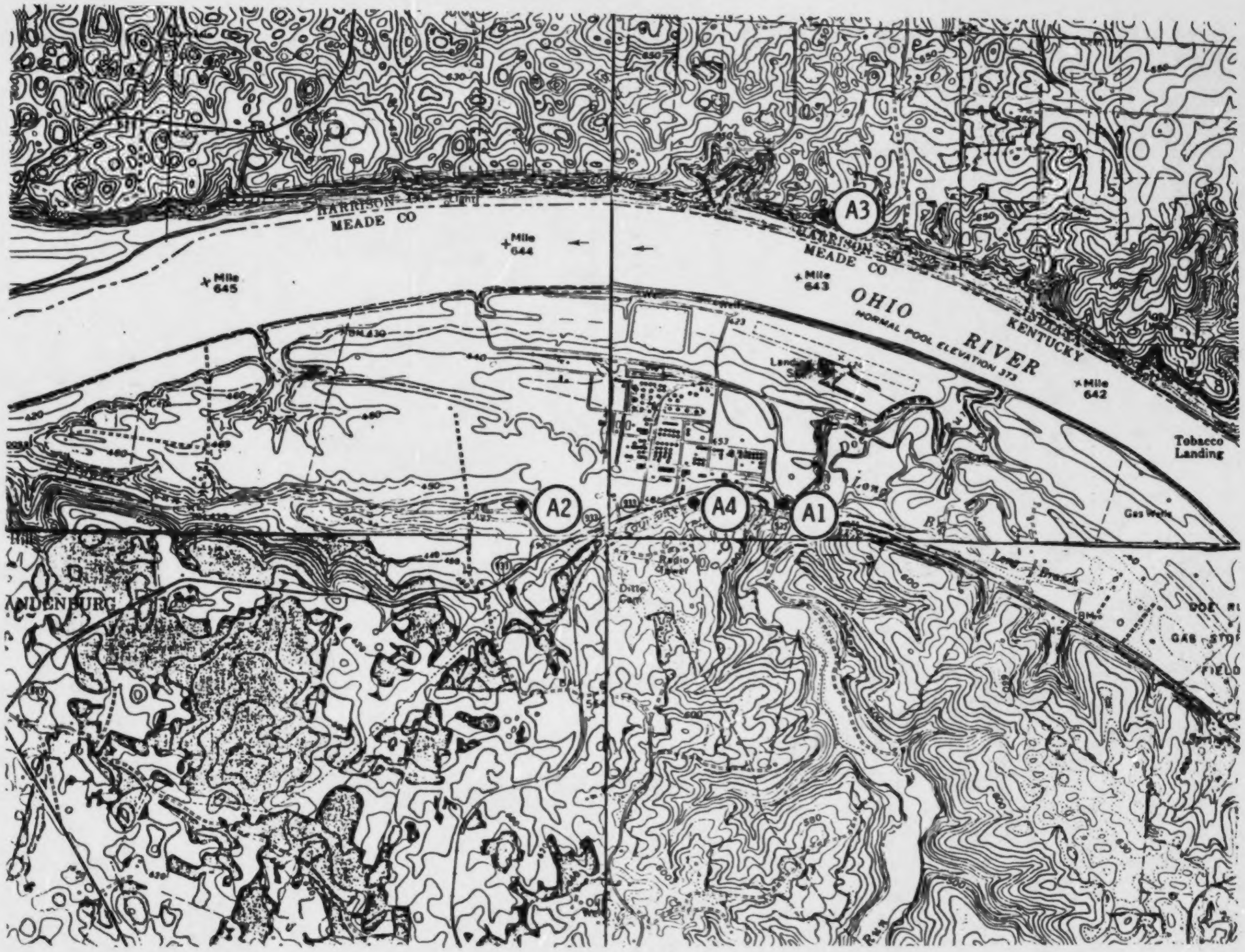

A3
HARRISON CO
MEADE CO
OHIO RIVER
NORMAL POOL ELEVATION 373
INDIANA
KENTUCKY
Mile 642
Mile 643
Mile 644
Mile 645
Tobacco Landing
Gas Wells
A1
A4
A2
BRANDENBURG

Figure 24. Air sampling sites - perimeter at Olin Corporation, Brandenburg, Kentucky.

TABLE 29. AIR SAMPLING AT OLIN CORPORATION BRANDENBURG, KY. ON 31 MARCH - 1 APRIL 1977

Sample (Tenax tube)	Location	Compass reading	Sampling Time Start	Sampling Time End	Duration, min	Volume, liter	β-chlorethers detected
A-1 (232)	Array #1	120	1100 (3-31)	1830 (3-31)	450	3.65	None
A-2 (243)	Array #2 ~ 800 m ESE of Olin	120	1100 (3-31)	1830 (3-31)	450	85.3	None
A-3 (233)	Array #3	120	1000 (3-31)	1830 (3-31)	450	137.0	None
A-4 (256)	Array #4	120	1100 (3-31)	1830 (8-31)	450	104.5	None
A-5 (246)	Background for Array ~ 640 m WSW of Olin	240	1135 (3-31)	1923 (3-31)	468	105.0	None
P-1 (251) (a)	North bank of Ohio River	0	1000 (4-1)	1800 (4-1)	480	~120	None
P-2 (254) (a)	N side of service road 0.3 km from Doe Run	240	1030 (4-1)	1820 (4-1)	480	~120	None
P-3 (235) (a)	S side of Doe Run Rd.	180	1050 (4-1)	1850 (4-1)	480	~120	None
P-4 (252) (a)	E side of Doe Run Rd.	120	1110 (4-1)	1910 (4-1)	480	~120	None

(a) Sampling start time, stop time and sampling volume for perimeter samples are approximate due to loss of sampling data sheets. Estimates shown in table are based on written record of verbal debriefing after sampling trip.

TABLE 30. WEATHER CONDITIONS DURING SAMPLING AT OLIN CORPORATION, BRANDENBURG, KY. 31 MARCH 1977

Time (Date)	Wind Speed, km/hr	 Direction, degrees
March 31, 1977		
1100	4.8	70
1130	8.1	20
1200	3.2	250
1230	4.8	230
1300	0	-
1330	3.2	90
1400	11.3	340
1430	8.1	350
1500	3.2	135
1530	3.2	340
1600	1.6	340
1630	9.7	350
1700	11.3	320
1730	0	-
1800	4.8	340
1830	0	-

Figure 25. The locations, sampling start, stop times, duration and volume are listed in Table 31. The samples were collected in polyethylene containers. Photographs of the outfall and two downstream sampling locations are shown in Figure 26.

The samples were extracted and analyzed as described in Section 5 and 6 except analysis was performed on a HP5982 GC/MS. None of the β-chloroethers were detected for these samples. Average detection limit for the four samples was 5 x 10^{-6} g/l. Analysis of the downstream #1 water sample concentrate was performed by scanned GC/MS. The presence of low levels of hydrocarbons was detected in the sample. Total organic carbon analysis of the four samples was also performed and results are reported in Table 32.

8.2.3 Soil Samples

A total of eleven soil samples were taken in the area of the Olin plant at Brandenburg, Ky. The soil sampling locations are shown in Figure 27. The samples were composite soil samples collected from soil cores and stored in polyethylene bags. The samples (50 g) were Soxhlet extracted with 5% ethyl ether in hexane and analyzed by GC/MS on a HP5982 GC/MS. None of the samples contained the six β-chloroethers of interest. Average detection limit for the soil samples was 8 x 10^{-6} g/g.

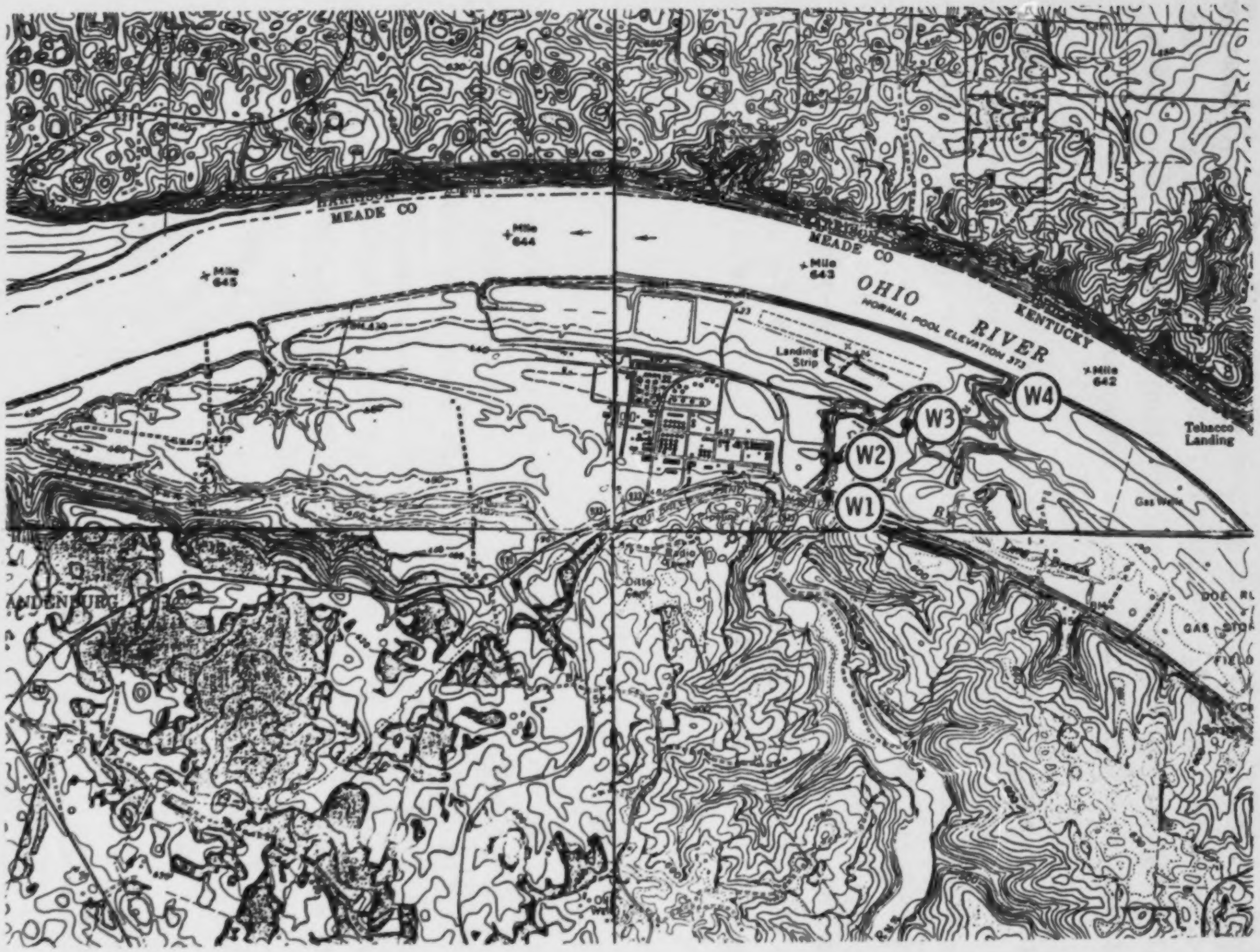

OHIO RIVER
NORMAL POOL ELEVATION 373
KENTUCKY
MEADE CO
MEADE CO
Mile 642
Mile 643
Mile 644
Mile 645
Landing Strip
Tobacco Landing
Gas Wells
W1
W2
W3
W4

Figure 25. Water sampling sites at Olin Corporation, Brandenburg, Ky.

TABLE 31. WATER SAMPLING AT OLIN CORPORATION BRANDENBURG, KY. ON 30-31 MARCH 1977

Sample (Tenax tube)	Location	Sampling				β-chloroethers detected
		Time		Duration, min	Volume, liter	
		Start	End			
W-1	Upstream - Doe Run ~ 0.2 km south of outfall	1635 (3-30)	1817 (3-31)	1542	~4	None
W-2	Outfall - Doe Run	1613 (3-30)	1100 (3-31)	1487	~4	None
W-3	Downstream #1 - Doe Run ~0.4 km north of outfall	1510 (3-30)	1639 (3-31)	1529	~4	None
W-4	Downstream #2 - Doe Run ~0.8 km north of outfall, 30 m south of Ohio River	1533 (3-30)	1615 (3-31)	1482	~4	None

(a) Outfall

4101-33
4101 34

(b) Downstream #1

(c) Downstream #2

Figure 26. Photographs of water sampling locations at Olin Corporation, Brandenburg, Kentucky.

TABLE 32. TOTAL ORGANIC CARBON ANALYSIS OF WATER SAMPLES FROM OLIN CORPORATION, BRANDENBURG, KENTUCKY

Sample	Total Organic Carbon, PPM
W-1 (upstream)	8.3
W-2 (outfall)	20.7
W-3 (downstream #1)	16.4
W-4 (downstream #2)	14.1

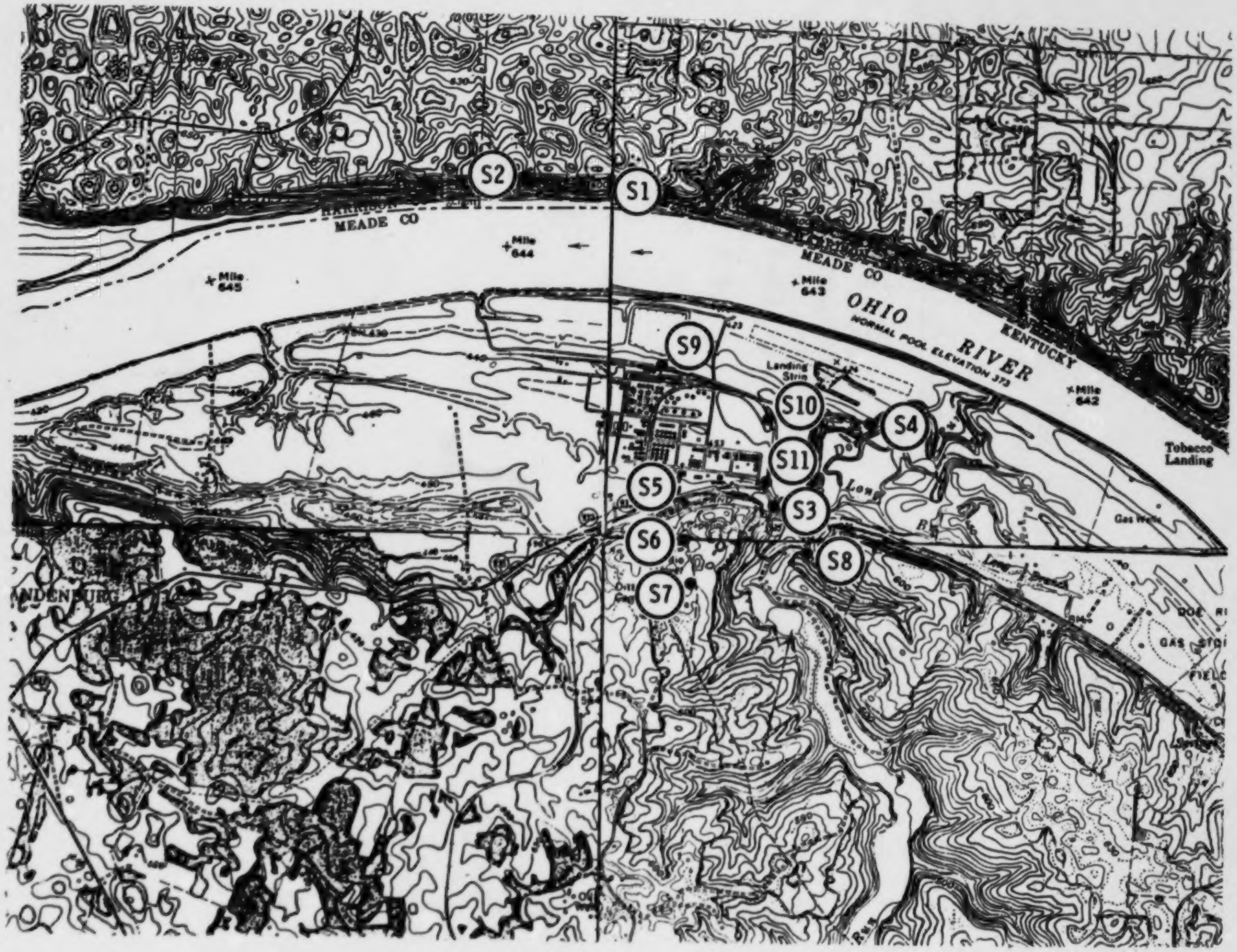

S1
S2
S3
S4
S5
S6
S7
S8
S9
S10
S11
MEADE CO
Mile 645
Mile 644
Mile 643
Mile 642
OHIO RIVER
NORMAL POOL ELEVATION 373
KENTUCKY
Landing Strip
Tobacco Landing
Gas Wells
Long Branch

Figure 27. Soil sampling sites at Olin Corporation, Brandenberg, Ky.

SECTION 9

SAMPLING AND ANALYSIS FOR β-CHLOROETHERS AT DOW CHEMICAL USA, FREEPORT, TEXAS

9.1 PRESAMPLING SURVEY

9.1.1 Description of the Plant Site

Dow Chemical USA, located on Texas Highways 288 and 332 (P.O. Box K) in Freeport, Texas, 77541 is a huge industrial chemical complex. Among the chemicals produced at this site are ethylene oxide (production capacity equals 9.07 x 10^7 kg/yr via chlorohydrin and 9.95 x 10^7 kg/yr via direct oxidation) and propylene oxide [production capacity equal 4.15 x 10^8 kg/yr via chlorohydrin (includes 9.07 x 10^7 kg/yr which is switchable to ethylene oxide production)]. By-products of the chlorohydrin processes for producing the oxides are bis(2-chloroethyl)ether and bis(2-chloroisopropyl)ether, respectively. Also produced at this location is epichlorohydrin (production capacity is 1.13 x 10^8 kg/yr). A possible by-product of this material is bis(1-chloromethyl-2-chloroethyl) ether.

Dow occupies four sites at Freeport, Texas. The four sites are Dow Chemical Plant A, Plant B and Oyster Creek Division and Dow Badische Company. The entire complex extends along Texas 332, 11.3 km from the northwest side of Plant B to the southeast side of Plant A. Figure 28 is a topographical map of the Freeport area with the location of the Dow property for Plants A and B indicated on the map. Telephone contacts

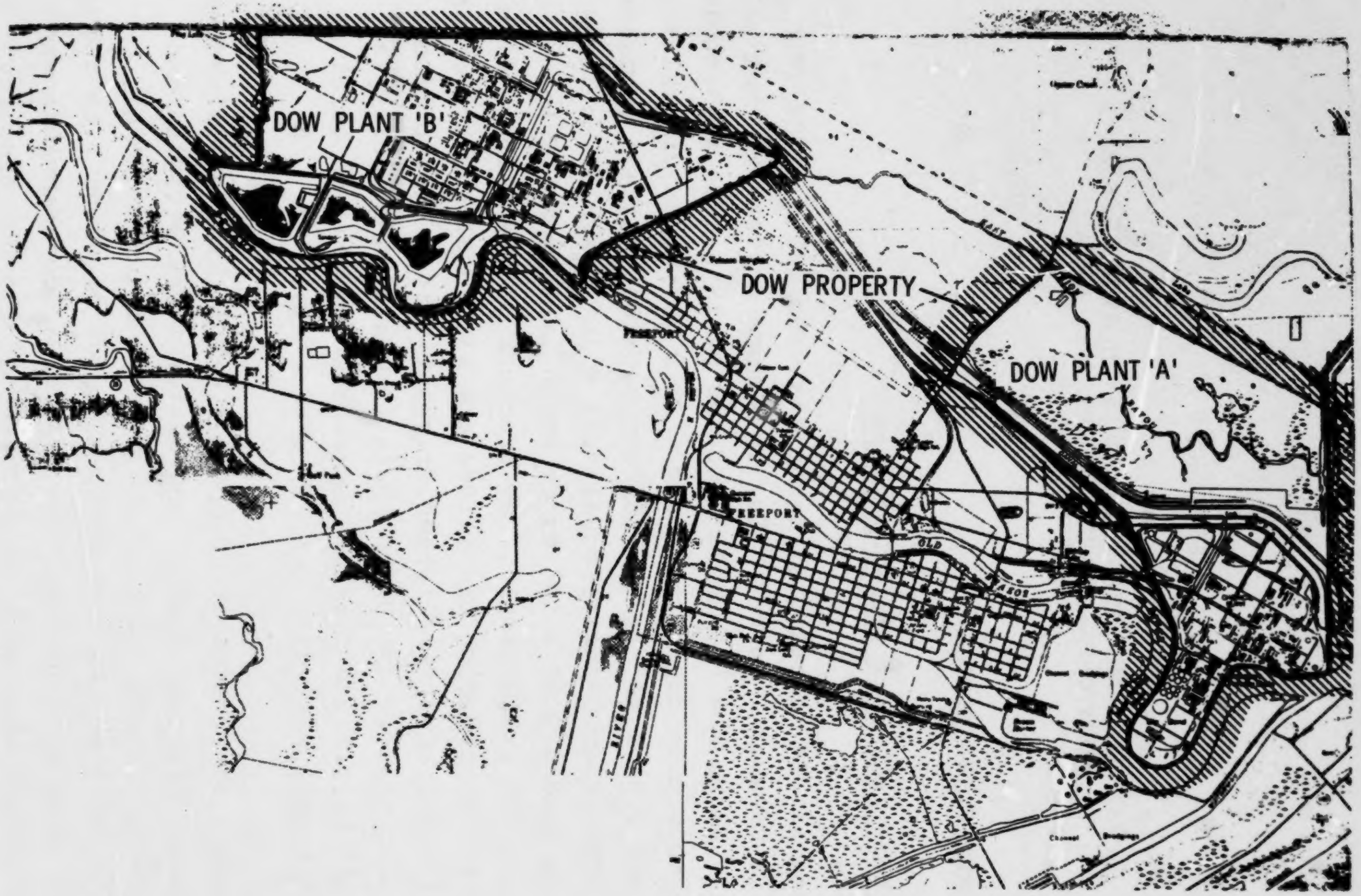

DOW PLANT 'B'
DOW PROPERTY
DOW PLANT 'A'
FREEPORT

Figure 28. Topographical map of Freeport area showing location of Dow Chemical, Plant A and Plant B.

with Texas air and water pollution control personnel indicated the ethylene and propylene oxide production facilities were located at Plant A. Liquid waste from both plants is treated at Plant B before disposal into the Brazos River.

A presurvey was performed on June 19, 1977. The presurvey consisted of a visual inspection of the entire complex, since contact with plant personnel was not allowed, and selection of sampling sites for air and water samplers.

The entire complex occupies the majority of an area of 11 km by 3.2 km. Dimensions for the Plant A site are shown on the topographical map in Figure 29. The Plant A site is a large number of buildings, oil and gas storage tanks, open construction distillation columns, cooling towers and flares. A panoramic photograph of Plant A, taken at the eastern edge of the Dow property, is shown in Figure 30. Plant A is almost entirely surrounded by water. All of the land inside the water is owned by Dow and some of the land outside the waste-ways is owned by Dow. These circumstances prevented air samplers being placed closer than 1 km from the center of the plant.

Dow Chemical, Plant A, is bounded on the north by the Dow Barge Canal and the East Union Bayou. The Bayou is owned by Dow up to a small canal which parallels Texas 332. To the west and southwest the plant is surrounded by the Old Brazos River and the city of Freeport. To the south, the Old Brazos River and the Intercostal Waterway form a boundary. On the east is where the Old Brazos, Intercostal Waterway and the Dow Barge Canal merge. Also in this area is a Corps of Engineers storm protection area.

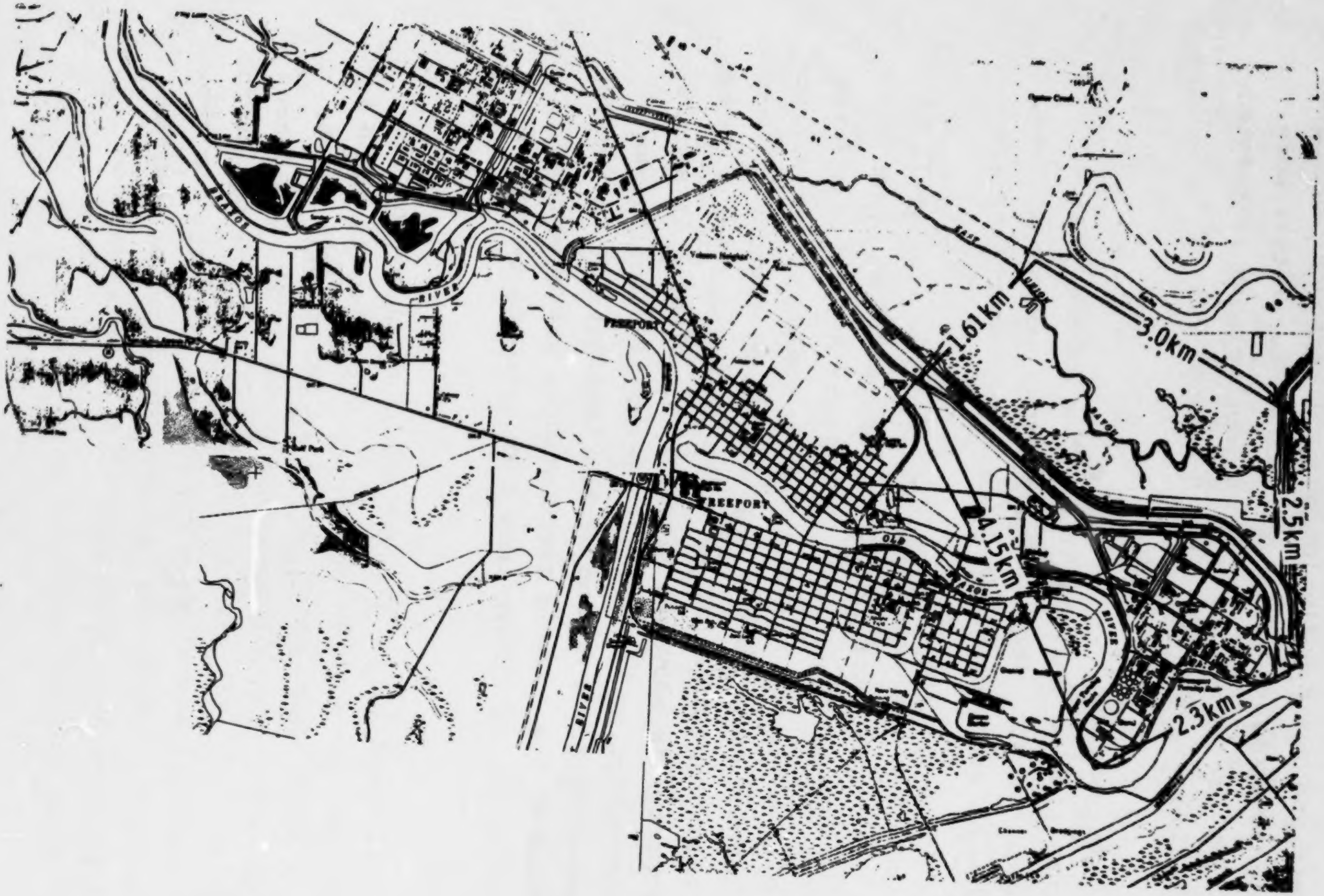

2.5km
3.0km
1.61km
4.15km
2.3km
FREEPORT
FREEPORT
BRAZOS
RIVER
OLD
RIVER

Figure 29. Topographical map showing dimension for Dow Chemical, Plant A.

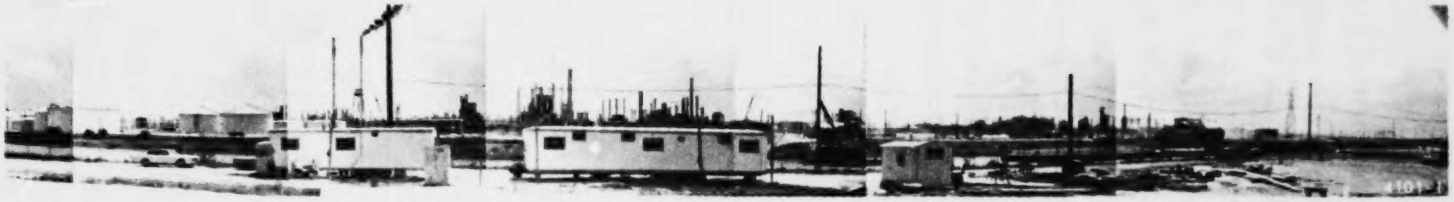


Figure 30. Composite panoramic photograph of Dow Chemical Plant A, Freeport, Texas.

9.1.2 Surrounding Area

The Freeport area is on the Texas Gulf coastal plain (130 km south of Houston). Elevation ranges from sea level to approximately 6 m above sea level. Vegetation in the area is mostly of the small (1-1.5 m) scrub bush-type with a few trees which are 4-5 m in height. The population of Freeport is 12,000. Clute, a town to the northwest, has a population of 6,000. Lake Jackson (population 13,400) is located northwest of Freeport approximately 12 km and Jones Creek, a small settlement (population 1300), is located west of Freeport. The other industries in the area are: A. P. Greene Refractories, Gulf Chemical and Metallurgical Corp., the Mill Creek Company, Mineral Research and Development, Nalco Chemical Company, Red Barn Chemicals, Inc., Rhodia, Inc., Shell Oil Buccaneer Plant, Shintech, Inc., Stauffer Chemical Co., and Schenectady Chemical Co. None of these industries are known to produce, emit or use β-chloroethers.

9.2 SAMPLING AND ANALYSIS RESULTS

Sampling of Dow Chemical U.S.A., Freeport, Texas was conducted on June 20-21, 1977. The conditions, locations and results for the air, water and soil samples collected during this sampling are contained in the following subsections.

9.2.1 Air Samples

Figure 81 is the topographic map of the Dow Chemical, Plant A area with the air sampling sites indicated on the map. The eight samplers employed were of the personnel samplers of the type described in Section 4.1. Large Tenax tubes described in the same section were used for sampling this site. Table 33 lists the sample numbers, the Tenax tube used, a description of the sampling location, the compass reading for the site relative to the center of Plant A, the starting and ending

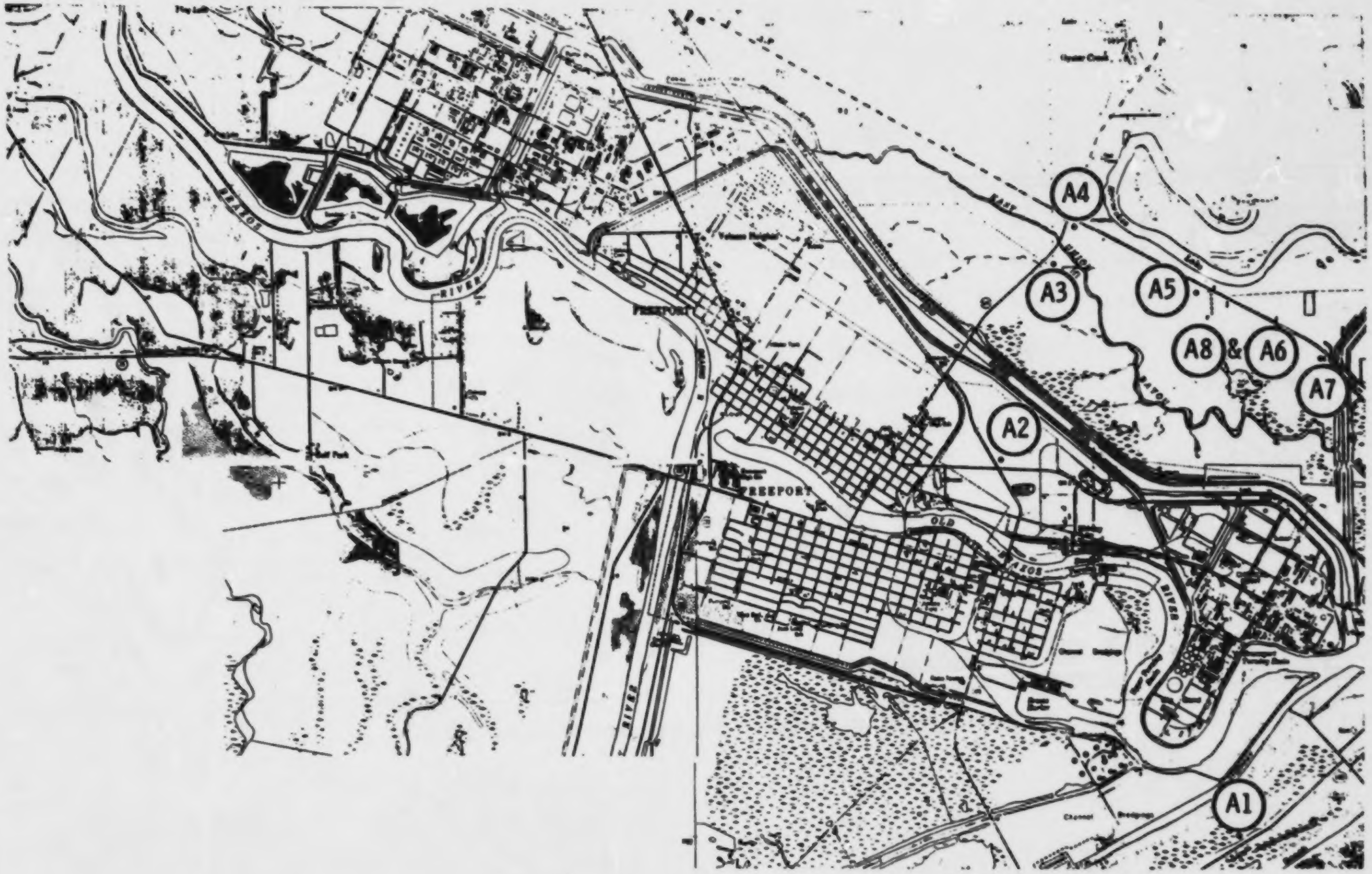

A1
A2
A3
A4
A5
A8 & A6
A7
FREEPORT
FREEPORT
BRAZOS
RIVER
OLD
RIVER

Figure 31. Location of air sampling sites at Dow Chemical, Freeport, Texas, June 20-21, 1977.

TABLE 33. AIR SAMPLING AT DOW CHEMICAL, FREEPORT, TX ON 20-21 JUNE 1977

Sample (Tenax tube)	Location	Compass reading	Sampling				β-chloroethers detected
			Time		Duration, min	Volume, l	
			Start	End			
A-1 (G-18)	Ouintana Island, TX 1495, 1.1 km NE of TX 1495 to the NW	180	1026 (6-20)	1821 (6-20)	475	475	None
A-2 (G-42)	NE side of TX 1495, I.0 km NW of Old Brazos River Bridge	275	1110 (6-20)	1910 (6-20)	480	480	None
A-3 (G-12)	E side of TX 523, 30 m from TX 523 0.3 km S of TX 332	325	1130 (6-20)	1923 (6-20)	473	473	None
A-4 (G-10)	S side of TX 332 0.3 km E of TX 523	325	1151 (6-20)	1947 (6-20)	476	476	None
A-5 (G-25)	S side of TX 332, 20 m S of TX 332, 1.2 km E of TX 523	330	1203 (6-20)	2001 (6-20)	478	478	None
A-6 (G-14)	S side of TX 332, 20 m S of TX 223, 2.3 km E of TX 523	350	1215 (6-20)	2012 (6-20)	477	477	None
A-7 (G-39)	S side of TX 332, 20 m S of TX 332, 2.9 km E of TX 523	15	1234 (6-20)	2028 (6-20)	474	474	None
A-8 (G-30)	S side of TX 332, 20 m S of TX 332, 2.3 km E of TX 523	350	2015 (6-20)	1236 (6-21)	981	981	None
A-9 (G-5)	Spiked - 100 μl of standard	-	-	-	-	-	See Section 7.2.1
A-10 (G-38)	Control	-	-	-	-	-	See Section 7.2.1

sampling times, duration of sampling, volume of gas sampled and β-chloroether(s) detected. Seven air samplers were deployed. Sampler A-1 served as a background. Samplers A-2 and A-7 formed an arc around the west and north side of the Dow Plant A perimeter. These seven samplers were run for approximately eight hours at a flow rate of one liter/min. Sample A-8 was collected at the same location as A-6 overnight. A-8 sampling time was 981 min. Wind speed and direction data for the sampling periods are listed in Table 34.

Air samples A-1, A-2, A-3, A-4, A-6, A-7, A-9 and A-10 were worked up by solvent desorbing the tubes with 4 ml of methanol. These samples were analyzed by gas chromatography/mass spectrometry, with the mass spectrometer operating in the selected ion monitoring (SIM) mode.

None of the six β-chloroethers of primary interest was detected in these samples (average detection limit = 7×10^{-7} g/m^3). Two air samples, A-5 and A-8, were thermally desorbed and analyzed with a GC/MS operating in the normal scanned mode (35-350 amu). Neither of these samples showed β-chloroethers of interest (average detection limit = 2×10^{-7} g/m^3) nor was any indication of bis(1-chloromethyl,2-chloroethyl) ether found in these samples. The total ion reconstructed chromatogram for sample A-8 is shown in Figure 32. Peaks in the chromatogram are also identified in Figure 32. The compounds found were:

trichlorofluoromethane
methylene chloride
3-methyl pentane
1,2-dichloroethane
trichloroethylene

TABLE 34. WEATHER CONDITIONS DURING SAMPLING AT DOW CHEMICAL, FREEPORT, TEXAS

Date (1977) and time	Wind Speed, km/hr	Wind Direction
20 June		
1000-1100	22.5	S
1100-1200	22.5	S
1200-1300	22.5	S
1300-1400	24.1	S
1400-1500	24.1	S
1500-1600	22.5	S
1600-1700	16.1	SE
1700-1800	22.5	S
1800-1900	22.5	S
1900-2000	24.1	S
2000-2100	22.5	S
2100-2200	22.5	S
2200-2300	25.8	S
2300-2400	20.9	S
21 June		
0000-0100	22.5	S
0100-0200	24.1	S
0200-0300	24.1	S
0300-0400	22.5	S
0400-0500	22.5	S
0500-0600	24.1	S
0600-0700	22.5	S
0700-0800	20.9	S
0800-0900	22.5	S
0900-1000	25.8	S

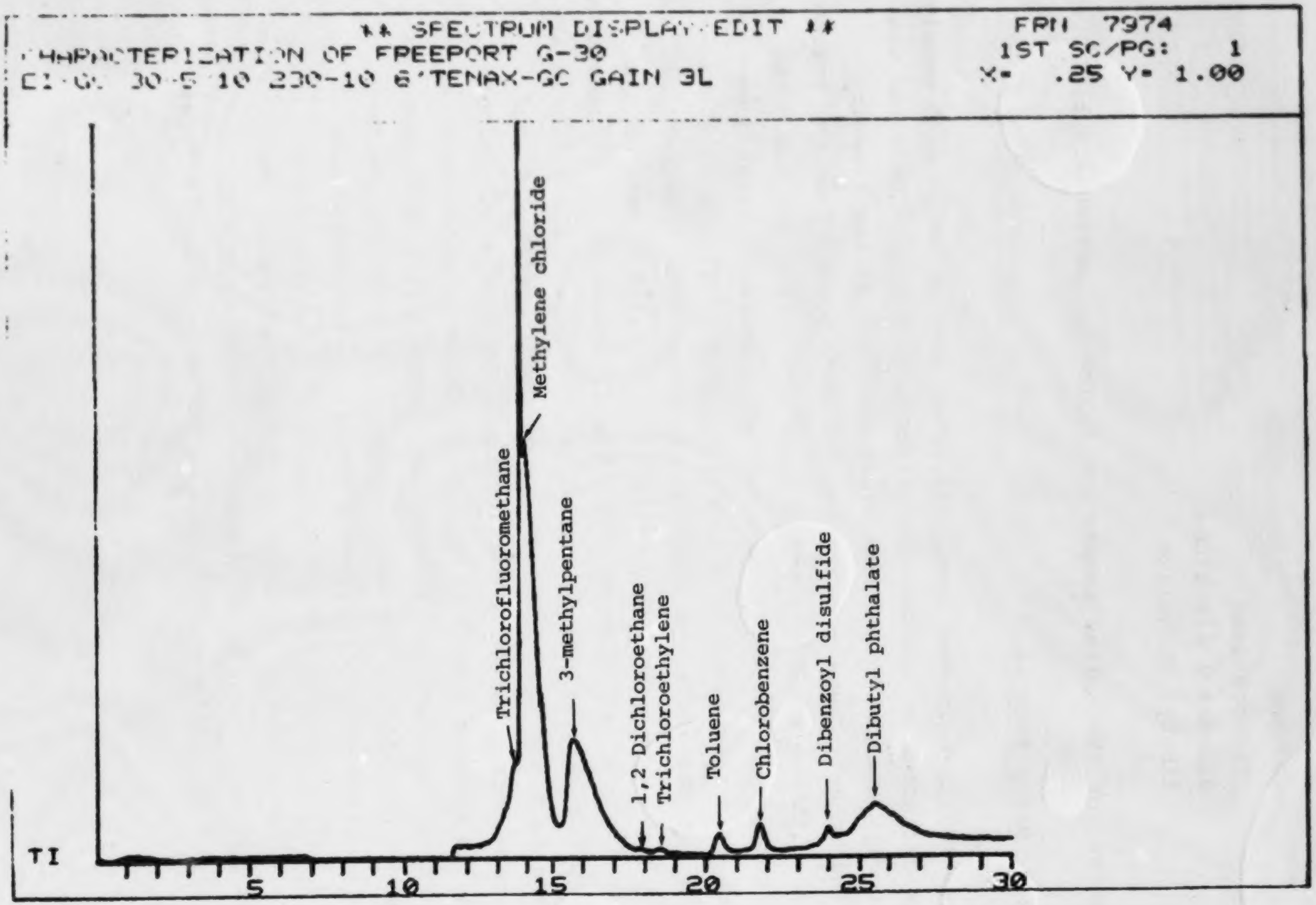


Figure 32. Total ion reconstructed chromatogram of Freeport Sample A-8.

toluene
chlorobenzene
dibenzoyl disulfude
dibutyl phthalate

Results for the spiked sample are listed in Section 7.2.1.

9.2.2 Water Samples

Three twenty-four hour composite water samples and 3 grab samples were collected at Dow Chemical, Freeport, Texas. The water was extremely clouded by reddish-brown sediment during sampling at the sites. The composite samples were pumped from the Brazos River with the toolbox sampler described in Section 4.2. The effluent from the sampler was collected in brown glass jugs which held approximately 4 liters of water. Figure 33 shows the locations where the samples were taken on a topographical map of the area. An exact description of each location, the times sampling was started and stopped, the duration of sampling, the approximate volume collected and β-chloroethers detected are listed in Table 35. Photographs of the downstream #2 and upstream locations are shown in Figure 34. The only sample found to contain a β-chloroether was the W-1 sample taken at downstream location #1 (nearest downstream point on Brazos River to Dow Plant B not on Dow property). The concentration of bis(2-chloroethyl)ether found in this sample was 1.8×10^{-6} g/liter. The concentrate of this same sample extract was analyzed by GC/MS in the scanned mode. The total ion chromatogram obtained is shown in Figure 35. the peaks identified. Compounds found in this sample were:

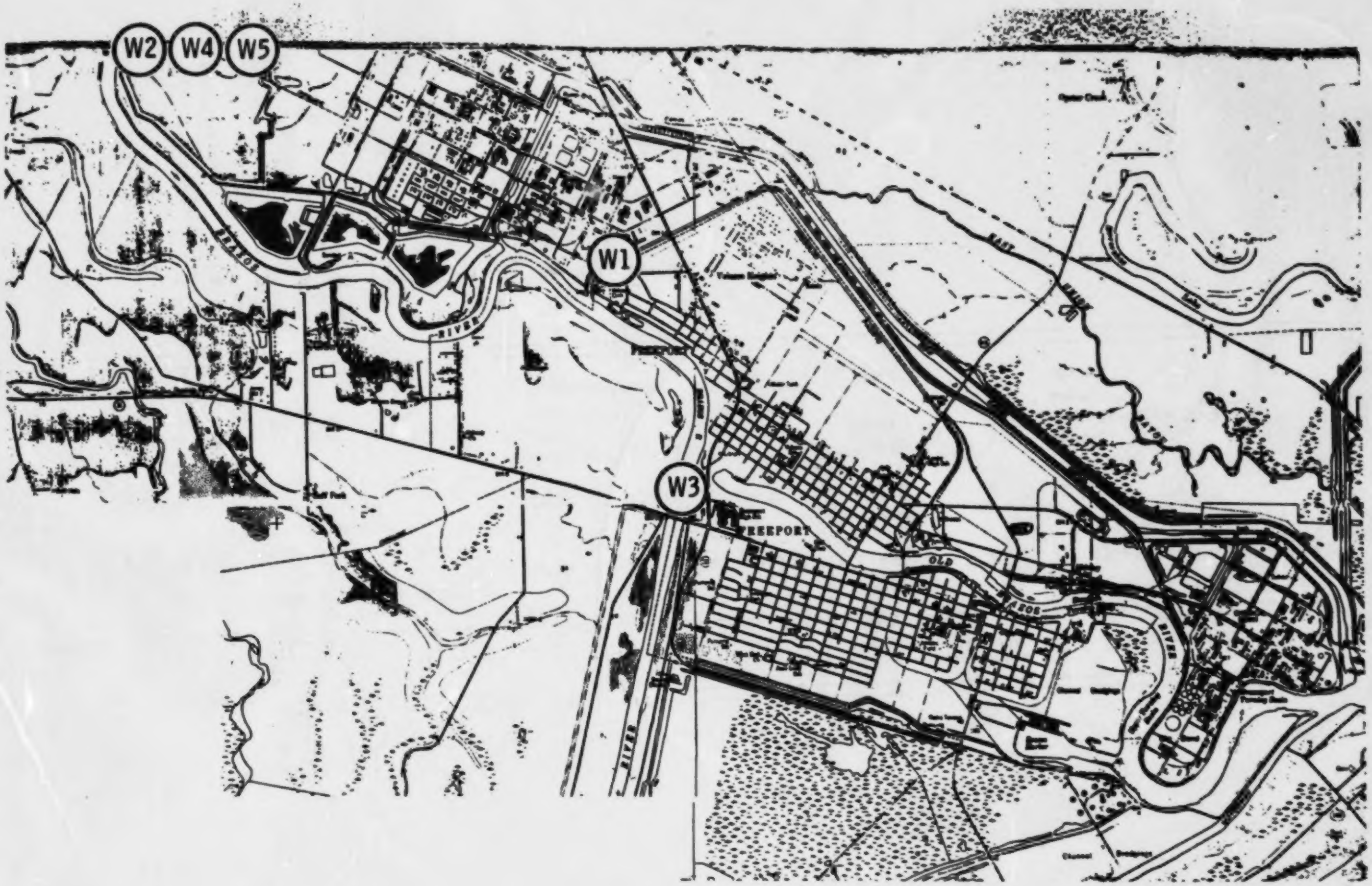
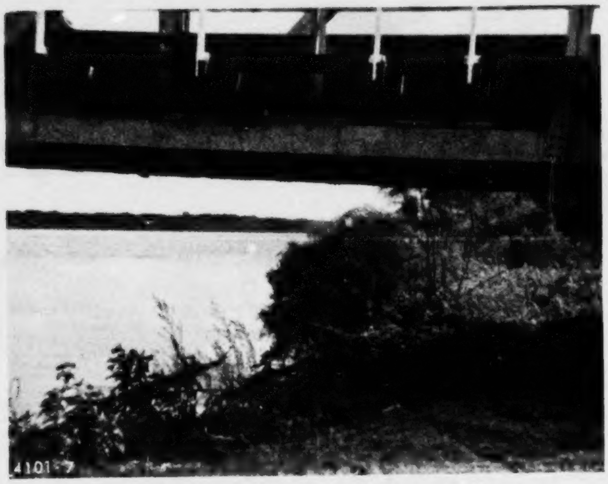

W2
W4
W5
W1
W3
FREEPORT
OLD
BRAZOS
RIVER

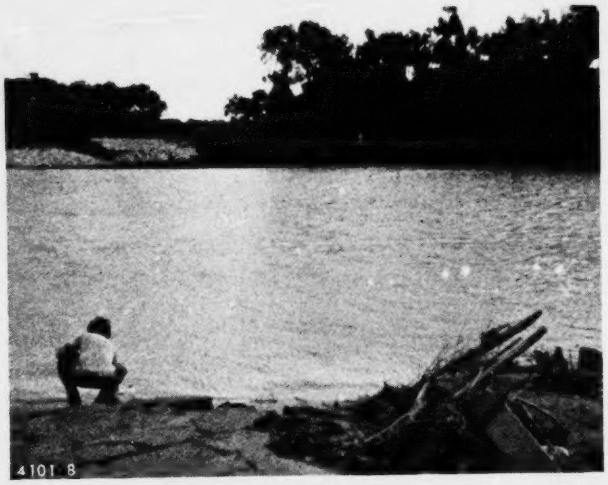
Figure 33. Water sampling sites at Dow Chemical, Freeport, Texas.

TABLE 35. WATER SAMPLING AT DOW CHEMICAL, FREEPORT, TX, 20-21 June 1977

Sample (Tenax tube)	Location	Sampling				β-chloroethers detected
		Time		Duration, min	Volume, l	
		Start	End			
W-1	N bank of Brazos River at Victoria St., 2.75 km NW of TX 36 bridge	0822 (6-20)	0822 (6-21)	1,440	4	Bis(2-chloroethyl) ether
W-2	S bank of Brazos River at side road from Brazos River Rd., 10.0 km NW of TX 36 bridge	0930 (6-20)	0930 (6-21)	1,440	4	None
W-3	E bank of Brazos River at TX 36 bridge	1000 (6-20)	1000 (6-21)	1,440	1	None
W-4	Same as W-2, spiked	0930 (6-21)	-	Grab	1	See Section 7.2.2
W-5	Same as W-2, control	0930 (6-21)	-	Grab	1	Lost
W-6	Same as W-3	1000 (6-21)	-	Grab		None



a. Downstream #2 at TX36 bridge.



b. Upstream

Figure 34. Photographs of two water sampling locations at Dow Chemical, Freeport, Texas.

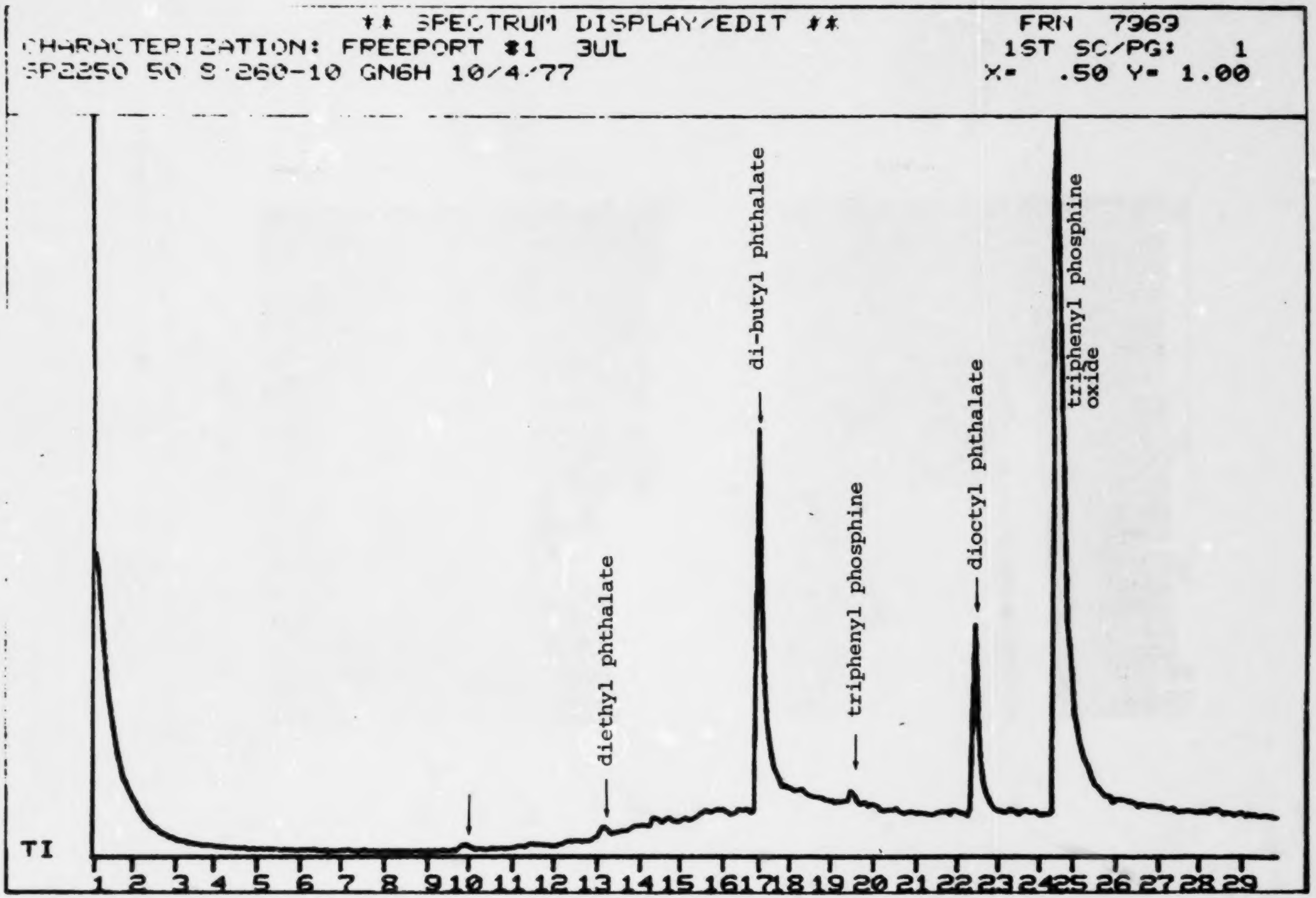


Figure 35. Total ion reconstructed chromatogam of water sample, W-1, Dow Chemical USA, Freeport, Texas.

diethyl phthalate
dibutyl phthalate
triphenyl phosphine
dioctyl phthalate
triphenyl phosphine oxide

Detection limit for the β-chloroethers in the other water samples was 2×10^{-7} g/liter of water.

Results for the spiked water sample are tabulated in Section 7.2.2.

9.2.3 Soil Samples

Figure 36 shows the locations for the soil samples which were taken at Dow Chemical, Freeport, Texas. The samples were collected in the downwind direction as indicated by the annual wind rose. A soil core 5 cm in diameter by 7.5 cm deep, weighing ∿ 350 g was taken at each site. Samples analyzed were S-4, S-5, S-6, S-7, and S-8. Fifty gram samples from each site were extracted. None of the β-chloroethers was found in these samples. Detection limits for the β-chloroethers was 4×10^{-9} g/g of soil. Results for the spike sample, S-14, are shown in Section 7.2.3.

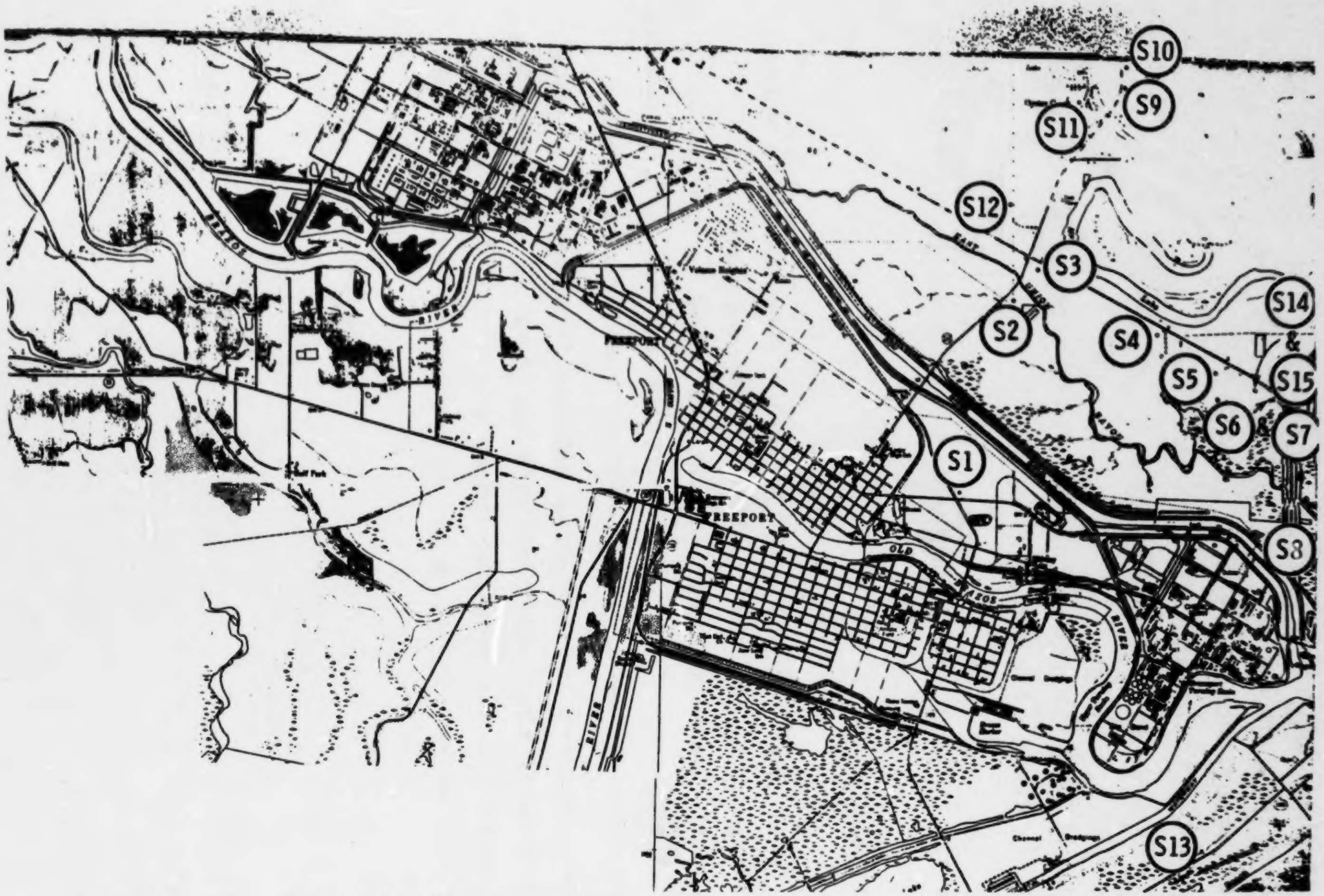

S10
S9
S11
S12
S3
S14
&
S2
S4
S5
S15
S6
&
S7
S1
S8
S13
FREEPORT
FREEPORT
BRAZOS
RIVER
OLD
BRAZOS
RIVER
RIVER

Figure 36. Soil samples locations at Dow Chemical, Freeport, Texas.

SECTION 10

SAMPLING AND ANAYSIS FOR β-CHLOROETHERS AT JEFFERSON CHEMICAL CO., INC., PORT NECHES, TEXAS

10.1 PRESAMPLING SURVEY

10.1.1 Description of the Plant Site

Jefferson Chemical Co., Inc. is located on Texas 366 (P. O. Box 847) in Port Neches, Texas, 77651. The plant produces a series of industrial organic chemicals. Among the materials produced at this site is propylene oxide (production capacity is 6.8×10^7 kg/yr) produced via the chlorohydrin route. A by-product of production of this product by the chlorohydrin process is bis(2-chloroisopropyl)ether. The Jefferson plant also produces ethylene oxide (production capacity is 2.15×10^8 kg/yr) via direct oxidation.

A presurvey was performed on June 21, 1977. The presurvey consisted of a visual inspection of the entire complex (since contact with plant personnel was not allowed) and selection of sampling sites for air and water samples.

Figure 37 shows the location of the Jefferson Chemical site in the Port Neches-Groves, Texas area topographical map. The entire complex occupies an area approximately 2 km square. The exact dimensions of the site are listed on the topographic map in Figure 38. Jefferson Chemical at Port Neches is a group of buildings, both open and closed construction, a large number

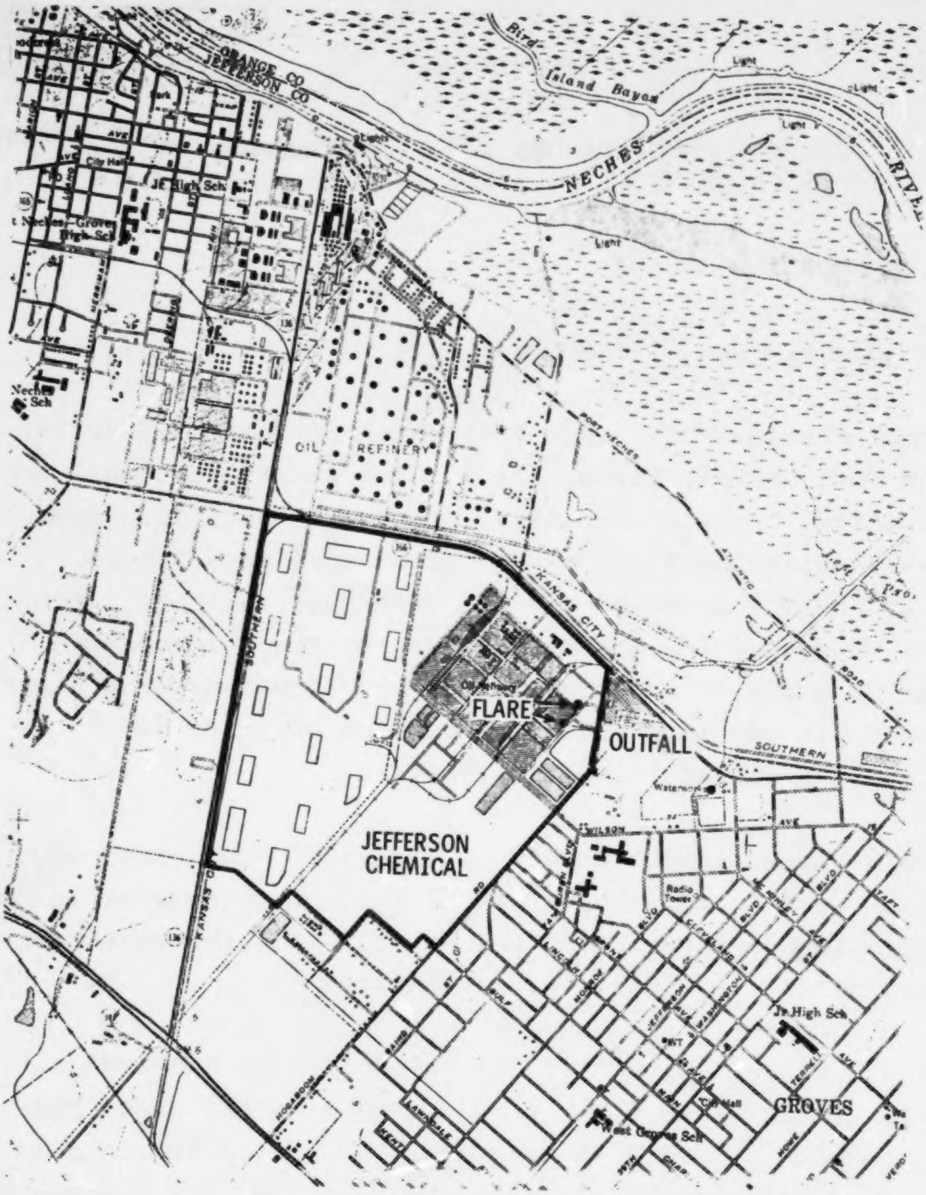

ORANGE CO
JEFFERSON CO
Bird Island Bayou
NECHES RIVER
Light
City Hall
Jr High Sch
Port Neches Groves High Sch
Neches Sch
OIL REFINERY
SOUTHERN
KANSAS CITY SOUTHERN
FLARE
OUTFALL
Waterworks
WILSON AVE
Radio Tower
JEFFERSON CHEMICAL
Jr High Sch
City Hall
West Groves Sch
GROVES

Figure 37. Jefferson Chemical location in Port Neches Groves, Texas.

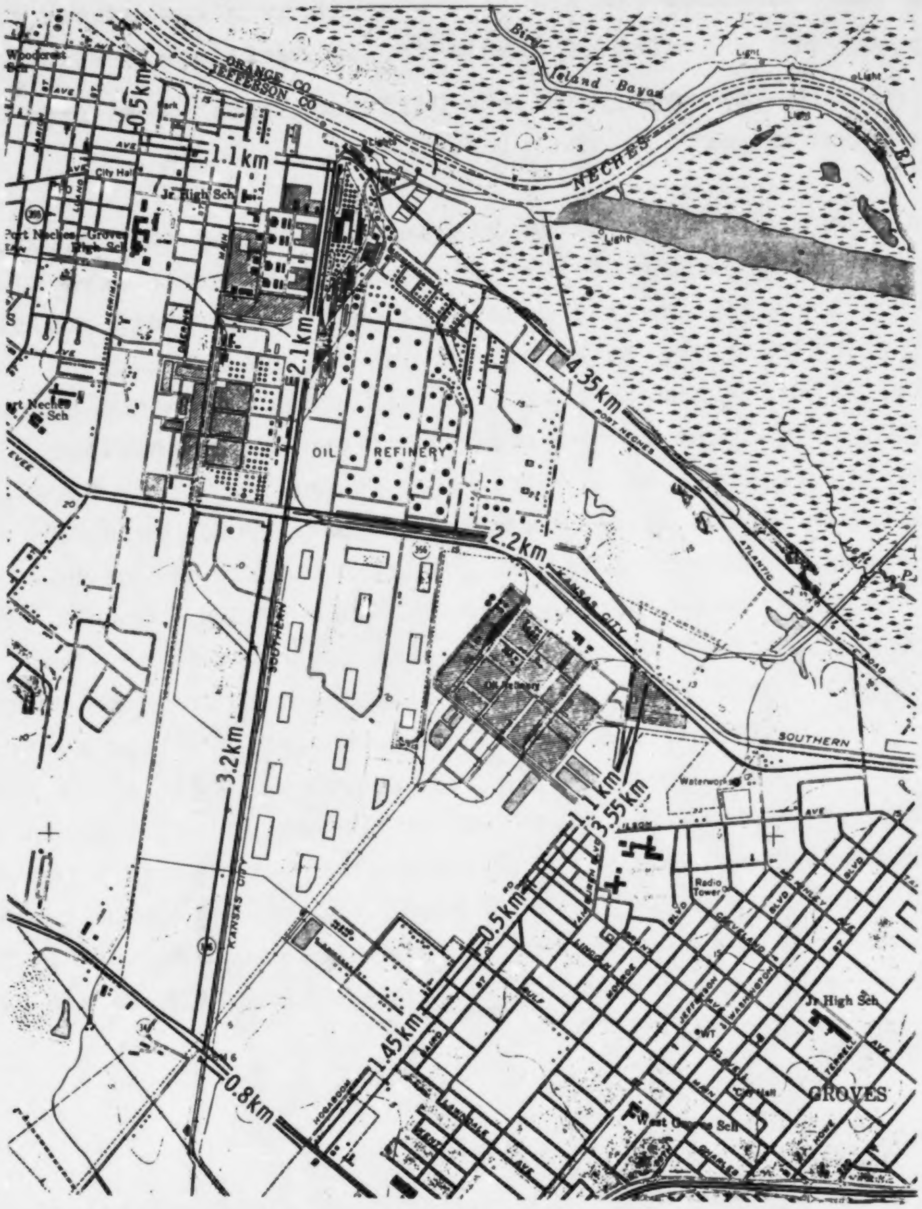

0.5km
1.1km
2.1km
4.35km
2.2km
3.2km
1.1km
3.55km
0.5km
1.45km
0.8km
ORANGE CO
JEFFERSON CO
NECHES
Bird Island Bayou
City Hall
Jr High Sch
Port Neches-Groves High Sch
Port Neches Sch
OIL REFINERY
Oil Refinery
SOUTHERN
KANSAS CITY
Waterworks
Radio Tower
Jr High Sch
GROVES
West Groves Sch

Figure 38. Dimension of area around Jefferson Chemical.

of oil storage tanks, spherical vessels for the storage of gases, distillation and cooling towers, and flares. The plant site is bounded on the north by Texas 366, on the east by Hogaboom Rd., on the west by Texas 136 and on the south by a wastewater treatment plant and a series of single-family dwellings. Figure 39 is a panoramic photograph of the Jefferson site taken from Orchard Avenue north of the plant.

As was true for all of the plants sampled during this study, the operating schedule of the processes of interest were unknown. The only visible emissions were steam vents and flares. One of the flares was extremely bright on the night of June 22, 1977. The entire area was illuminated by the flare and attempts to take pictures of the flare tower resulted in totally exposed film. Operations at the plant may have been abnormal due to the explosion of an ammonia tank truck on the plant property on June 17, 1977. The explosion destroyed one flare tower but otherwise did not seem to have interrupted operations. A slightly sweet odor was present in the area of the plant. Two large holding ponds are visible from Hogaboom Road in the Jefferson complex. During the presampling survey and sampling periods no water effluent was observed to be leaving the plant via a drainage ditch, which passes under Hogaboom Road, and parallels Texas 366. The ditch is then joined by a water flow from the Groves Texas Water Works and passes under Texas 366 and merges with water from other industries to form Left Prong. Left Prong then passes under Port Neches-Atlantic Road and then enters the Neches River.

10.1.2 Surrounding Area

The Port Neches-Groves area is on the Texas Gulf coastal plain in extreme southeastern Texas (approximately 30 km southeast of Beaumont). The elevation of the area ranges from 2 m to 6 m

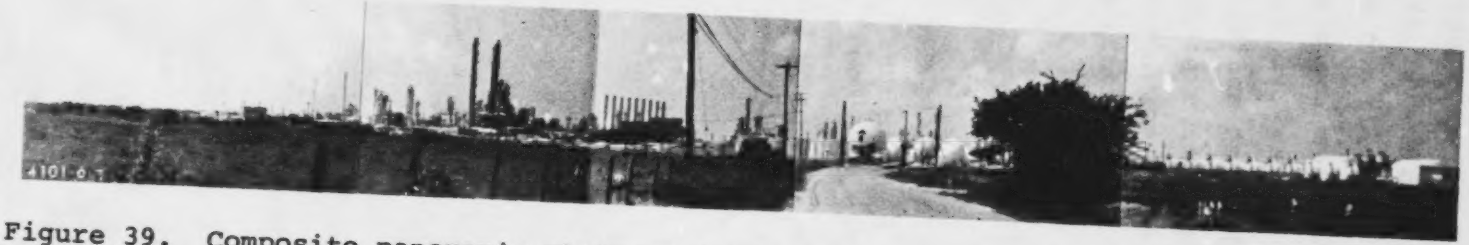


Figure 39. Composite panoramic photograph of Jefferson Chemical at Port Neches, Texas.

above sea level. Jefferson Chemical is located in Jefferson ounty, Texas. To the east and southeast are the towns of Port Arthur (population 57,000) and Groves (18,000); to the west and north are Port Neches (11,000) and Nederland (16,800). The other industries in the area include a large Texaco oil refinery, Bayou Pipe Line System Tank Field and a lumberyard north of Jefferson. To the east and northwest are Du Pont, B. F. Goodrich and National Butane plants. The vegatation in the area consists of small scrub trees, a few large planted trees,and marshy areas in the region along the Neches River.

10.2 SAMPLING AND ANALYSIS RESULTS

Sampling of the area around Jefferson Chemical, Port Neches, Texas for β-chloroethers was conducted on June 22-23, 1977. The conditions, locations and results for the air, water, soil and sediment samples collected during this sampling are contained in the following subsections.

10.2.1 Air Samples

Figure 40 is a topographic map showing the location of air sampling sites around the Jefferson Chemical Plant at Port Neches, Texas. A description of the sampling locations, compass readings relative to the center of the Jefferson plant, start and stop times, duration of sampling, sample volume and β-chloroethers detected are listed in Table 36. Sampling was accomplished using portable personnel samplers, large Tenax tubes and charcoal backup tubes described in Section 4.1. Weather conditions during the sampling period were very good. The temperature ranged from 24°C at night to 35°C during the day. The relative humidity was high, but no rain occurred during the sampling period. Wind speed and direction data supplied by the weather bureau at Jefferson County Airport are shown in Table 37. The wind was primarily from the south to southeast at 9 to 24 km/hr.

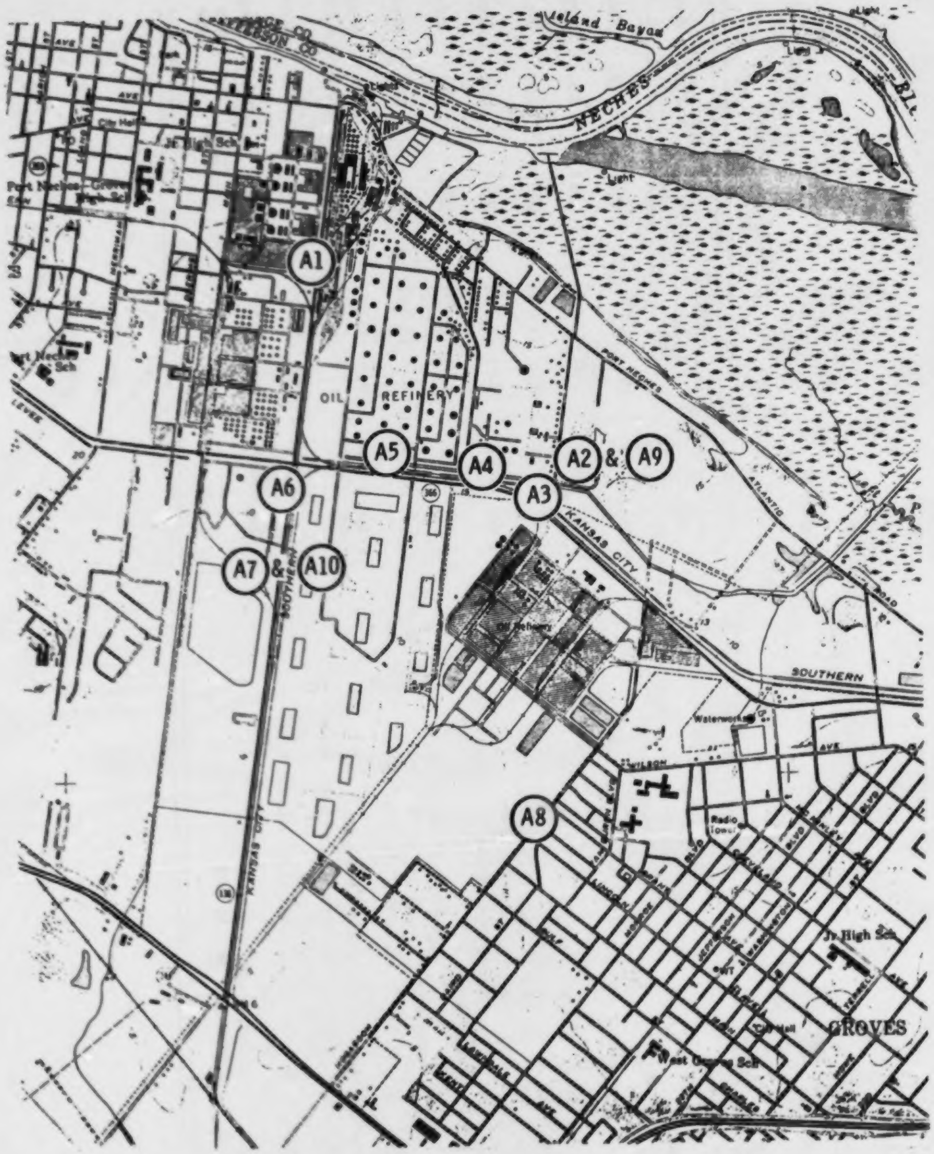

JEFFERSON CO
Island Bayou
NECHES
Light
City Hall
Jr High Sch
Port Neches-Groves High Sch
A1
OIL REFINERY
PORT NECHES
A5
A4
A2
&
A9
A6
A3
KANSAS CITY
ATLANTIC
A7
&
A10
SOUTHERN
Oil Refinery
SOUTHERN
Waterworks
WILSON
AVE
A8
Radio
Jr High Sch
GROVES
West Groves Sch
KANSAS CITY SOUTHERN

Figure 40. Air sampling sites at Jefferson Chemical, Port Neches, Texas.

TABLE 36. AIR SAMPLING AT JEFFERSON CHEMICAL, PORT NECHES, TX, ON 22-23 JUNE 1977

Sample (Tenax tube)	Location	Compass reading	Sampling				β-chloroethers detected
			Time		Duration, min	Volume, l	
			Start	End			
A-1 (G-34)	W side of TX 136, 1.1 km N of TX 366	0	1024 (6-22)	1824 (6-22)	480	480	None
A-2 (G-28)	E side of Orchard Ave., 0.16 km N of TX 366	350	1036 (6-22)	1836 (6-22)	480	480	None
A-3 (G-41)	N side of TX 366, 1.29 km E of TX 136	335	1047 (6-22)	1847 (6-22)	480	480	None
A-4 (G-23)	N side of TX 366, 1.1 km E of TX 136	320	1057 (6-22)	1857 (6-22)	480	480	None
A-5 (G-41)	N side of TX 366, 0.64 km E of TX 136	310	1104 (6-22)	1904 (6-22)	480	480	None
A-6 (G-24)	W side of TX 136, 0.16 km S of TX 366	295	1112 (6-22)	1913 (6-22)	481	481	None
A-7 (G-26)	W side of TX 136, 0.64 km S of TX 366	280	1119 (6-22)	1919 (6-22)	480	480	None
A-8 (G-17)	NW side of Hogaboom Road	180	1134 (6-22)	1934 (6-22)	480	480	None
A-9 (G-6)	E side of Orchard Ave., 0.16 km N of TX 366	350	1824 (6-22)	0845 (6-23)	843	843	None
A-10 (G-32)	W side of TX 136, 0.64 km S of TX 366	280	1921 (6-22)	0838 (6-23)	797	797	None
A-11 (G-21)	Spiked tube	-	-	-	-	-	See Section 7.2.1
A-12 (G-13)	Control tube	-	-	-	-	-	See Section 7.2.1

TABLE 37. WEATHER CONDITIONS DURING SAMPLING AT JEFFERSON CHEMICAL, PORT NECHES, TEXAS (COURTESY WEATHER BUREAU, JEFFERSON COUNTY AIRPORT) 24°C-35°C

Date (1977) and time	Speed, km/hr	Direction, degrees
22 June		
0955	11.7	170
1056	18.5	170
1158	20.4	170
1255	22.2	190
1356	20.4	180
1455	24.1	160
1555	22.2	180
1655	22.2	160
1755	24.1	180
1855	20.4	170
1955	16.7	180
2055	13.0	180
2155	11.1	160
2253	9.3	130
2347	11.1	120
23 June		
0053	13.0	120
0153	14.8	140
0256	11.1	150
0355	13.0	140
0457	11.1	150
0551	13.0	130
0655	11.1	160
0755	13.0	150
0855	16.7	150

Eight samplers were placed around the perimeter of the plant on June 22, 1977 and run for eight hours at 1.0 liter/min. Sampler A-8 was the background sampler. Samples A-1 through A-7 were situated on the rights of way along Texas 136, 366 and Orchard Avenue to the north and west of the plant. Samples A-9 and A-10 were collected during the night of June 22-23, 1977.

Air samples A-1, A-2, A-3, A-5, A-6, A-7, A-8 and A-10 were desorbed with methanol and analyzed by selected ion monitoring gas chromatography/mass spectrometry. No responses were found during the analysis of these seven samples for the six β-chloroethers of interest (average detection limit = 7×10^{-7} g/m^3). The two remaining air samples A-4 and A-9 were thermally desorbed and analyzed via GC/MS with the mass spectrometer operating in the scan mode (35-350 amu). Sample A-4 was lost during analysis. Sample A-9 showed none of the β-chloroethers of interest (average detection limit $\sim 2 \times 10^{-7}$ g/m^3).

The total ion reconstructed chromatogram for sample A-9 is shown in Figure 41. Peaks in the chromatogram are also identified in Figure 41. The compounds found were:

- methylene chloride
- toluene
- chlorobenzene

Results for the spiked sample tube are listed in Section 7.2.1.

10.2.2 Water Samples

Three 24-hour composite water samples and two grab water samples were collected on June 22 and Jund 23, 1977 at Jefferson Chemical, Port Neches, Texas. The drainage ditch from Jefferson was coated with an oily scum and was reddish-

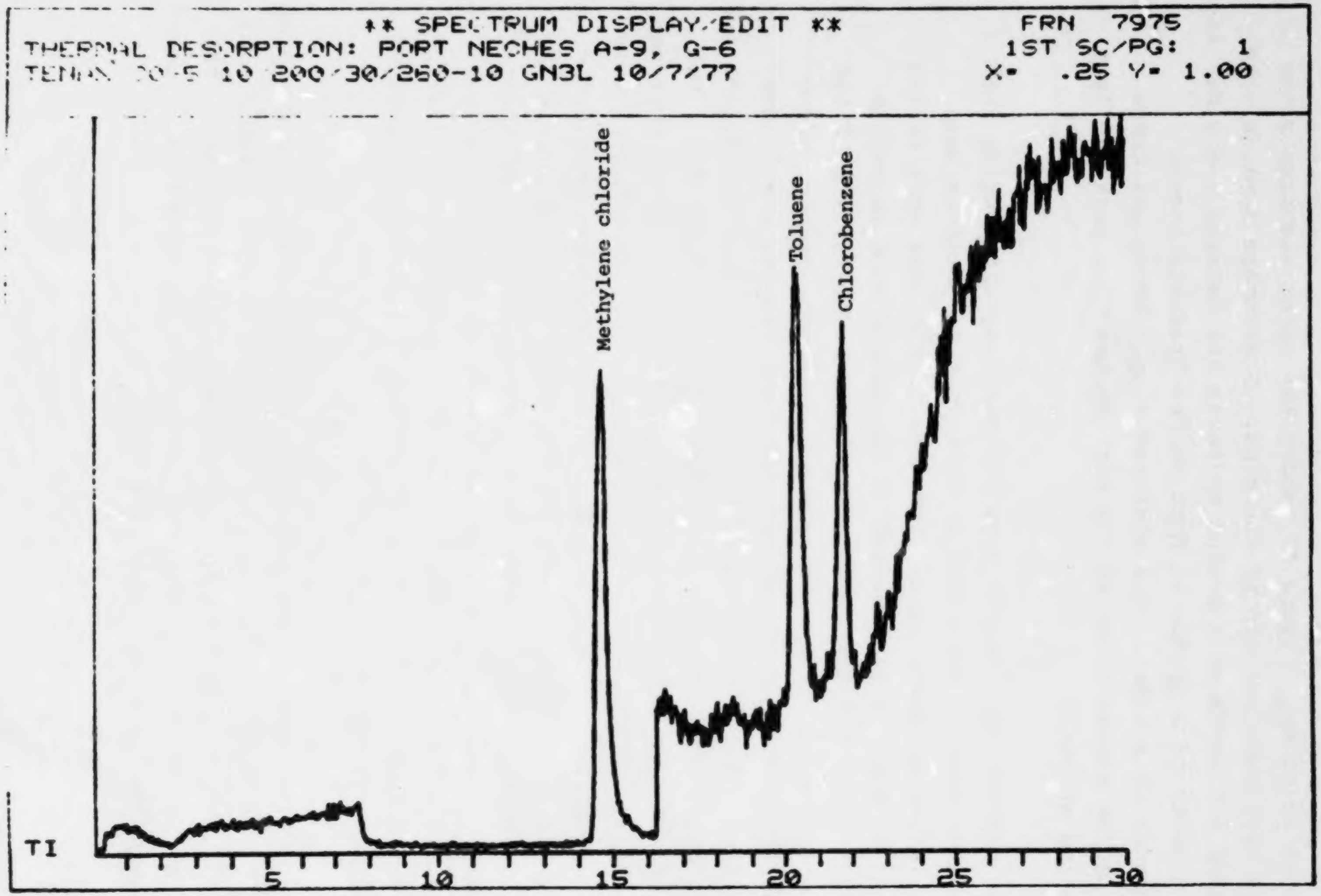


Figure 41. Total ion reconstructed chromatogram of Port Neches air sample A-9.

brown in color. Figure 42 shows the water sampling sites on the topographical map of the area. Downstream samples were taken 6 m north of a bridge on Texas 366 (stream 5 m wide) and 3 m south of a bridge on Port Neches-Atlantic Avenue (stream 10 m wide). The upstream sample which was taken from the Neches River at the Port Neches City park was lost during shipment.

The samples were pumped from the sampling sites using the toolbox sampler described in Section 4.2. Samples were collected in amber jugs. The caps of the jugs were teflon lined. Samples were placed in ice chests with styrofoam and ice and air freighted to Dayton. A description of the sampling site, times of sampling, duration, sample volume and β-chloroethers found for the water samples are listed in Table 38. Photographs of the outfall, drainage ditch, and two downstream sampling sites are shown in Figure 43. One liter of each sample was extracted with three 100 ml portions of methylene chloride. The methylene chloride extracts were then combined and evaporated in a Kuderna-Danish evaporator to ∿ 2.5 ml. Analysis was performed by GC/MS/SIM. Only the downstream #1 sample (W-1) showed a β-chloroether of interest. Bis(2-chloroisopropyl) ether was found in this sample (W-1) at a concentration of 2.2×10^{-5} g/liter. The detection limit for the other downstream sample was 2×10^{-7} g/liter for each of the six β-chloroethers.

The concentrate of the downstream #1 water sample was analyzed by GC/MS in the normal scanned mode on a SP 2250 column. The total ion chromatogram obtained is shown in Figure 44. The peaks in the chromatogram are identified in Figure 44. Compounds found in this sample were:

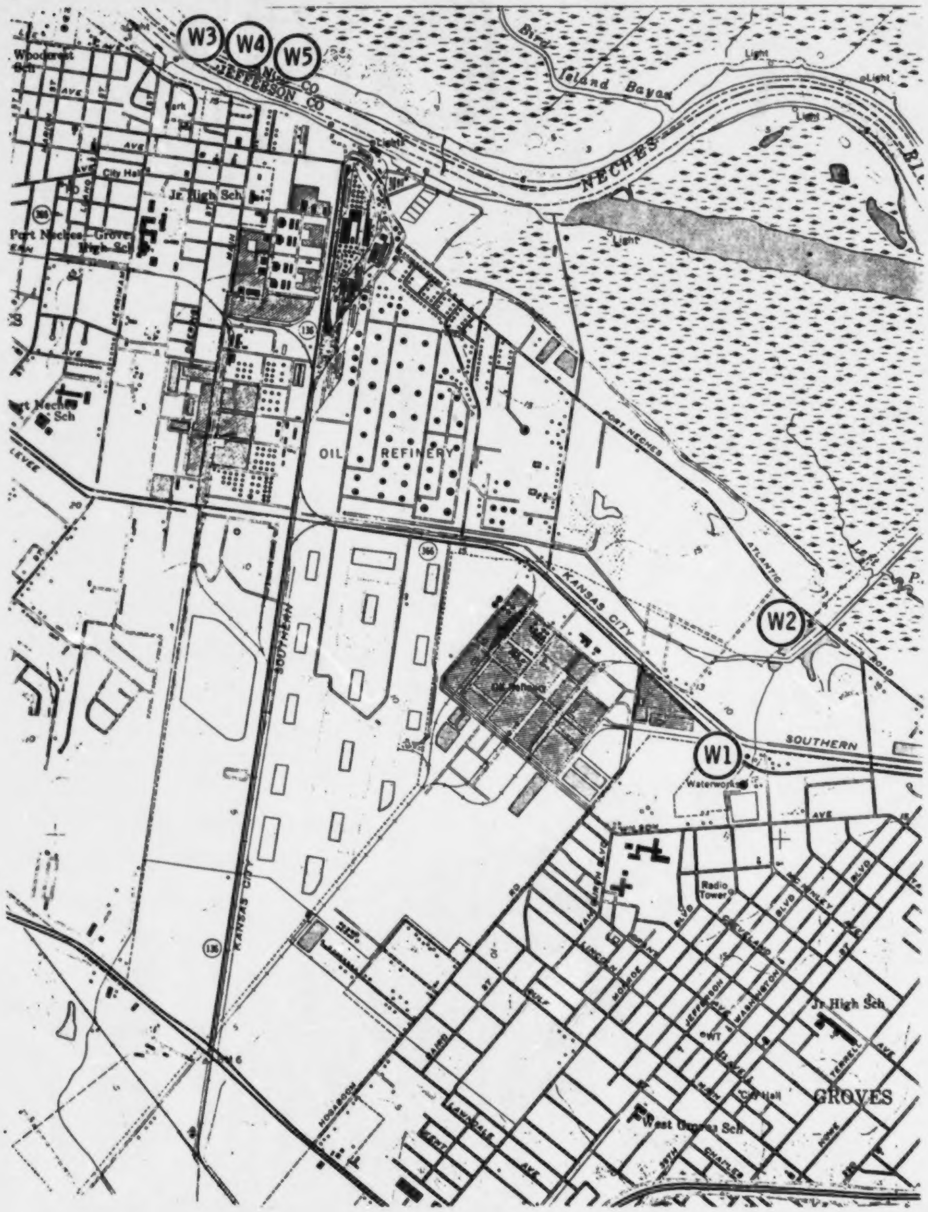
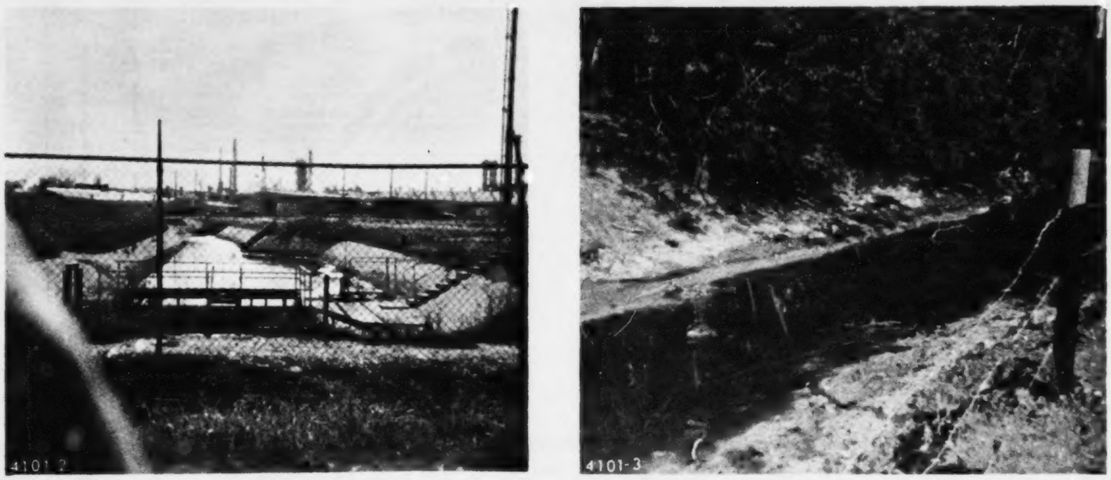

W3
W4
W5
W2
W1
JEFFERSON CO
NECHES
Bird Island Bayou
OIL REFINERY
Oil Refinery
KANSAS CITY
SOUTHERN
Port Neches-Groves High Sch
Jr High Sch
City Hall
Port Neches Sch
Waterworks
Radio Tower
Jr High Sch
GROVES
West Groves Sch
City Hall

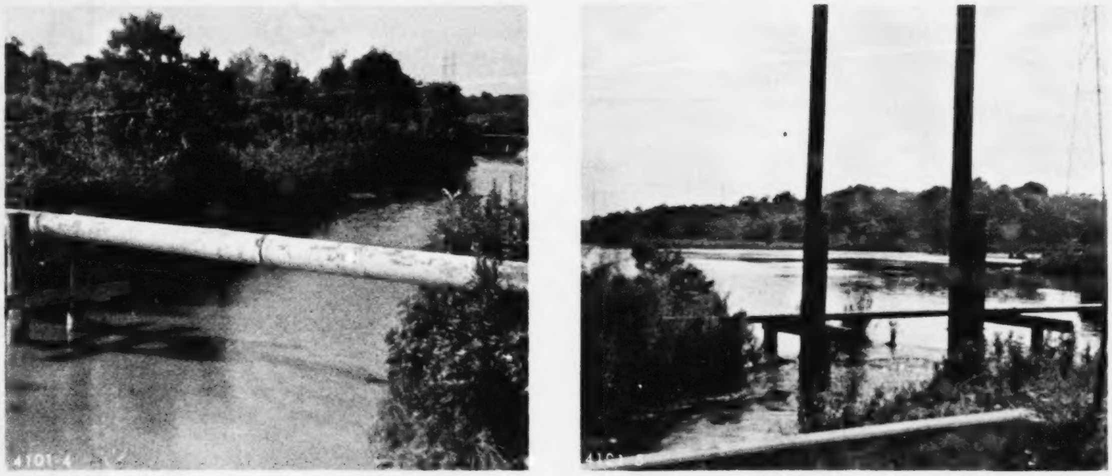
Figure 42. Water sampling sites at Jefferson Chemical, Port Neches, Texas.

TABLE 38. WATER SAMPLING AT JEFFERSON CHEMICAL, PORT NECHES, TX, ON 22-23 JUNE 1977

Sample (Tenax tube)	Location	Sampling				β-chloroethers detected
		Time		Duration, min	Volume, l	
		Start	End			
W-1	N side of TX 366, 0.8 km E of Hogaboom Road	0857 (6-22)	0857 (6-23)	1,440	∿4	BCIPE
W-2	S side of Port Neches - Atlantic Rd., 4.2 km SE of TX 136	0919 (6-22)	0919 (6-23)	1,440	∿4	None
W-3	S bank of Neches River at Port Neches City Park	1012 (6-22)	1012 (6-23)	1,440	∿4	None
W-4	Same as 3 Spiked	Grab	1012 (6-23)	-	∿1	See Section 7.2.2
W-5	Same as 3	Grab	1012 (6-23)	-	∿1	See Section 7.2.2



a. Outfall b. Drainage ditch



c. Downstream sampling point #1 d. Downstream sampling point #2

Figure 43. Photograph of Jefferson Chemical, Port Neches, Texas. Water outfall and downstream sampling location.

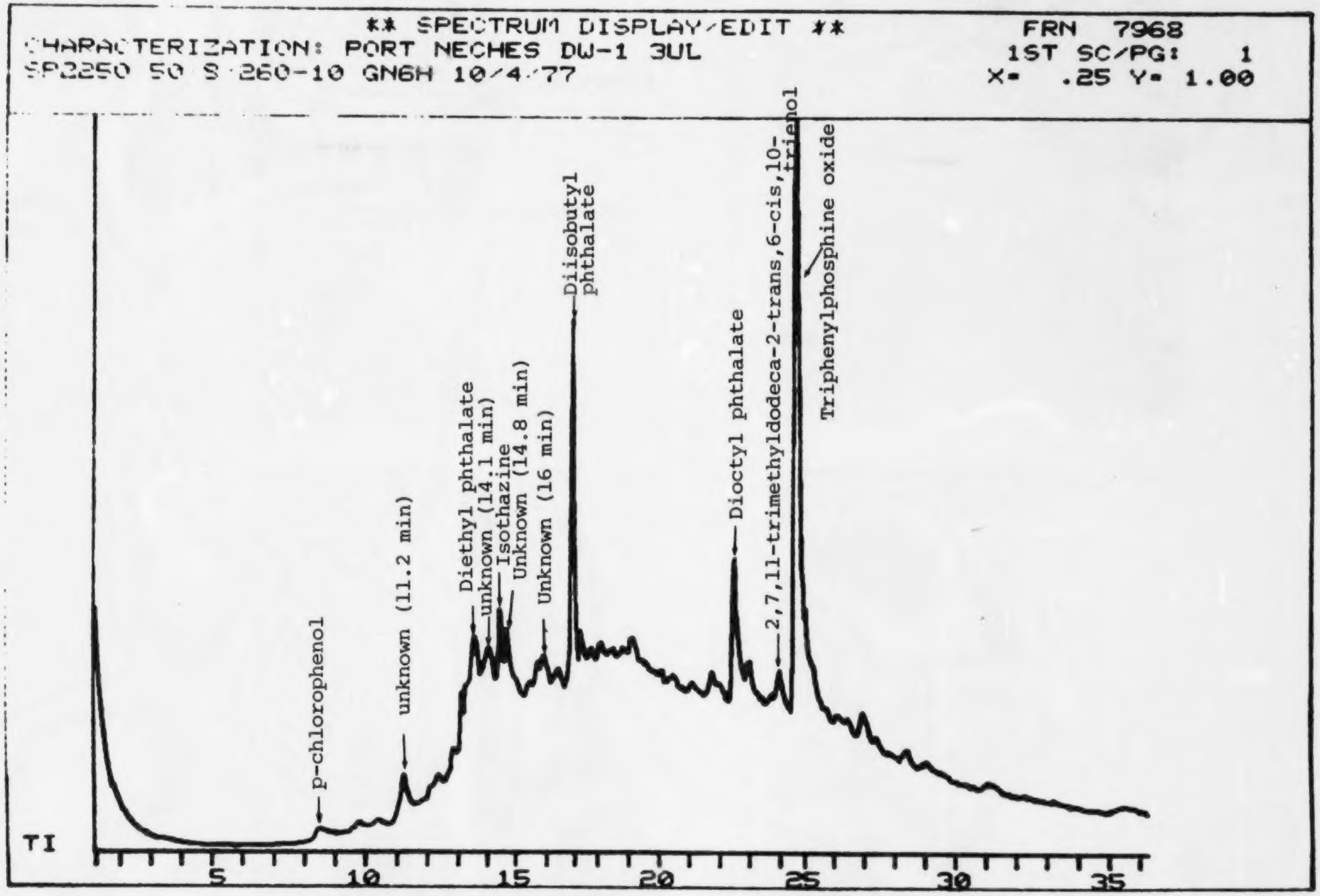


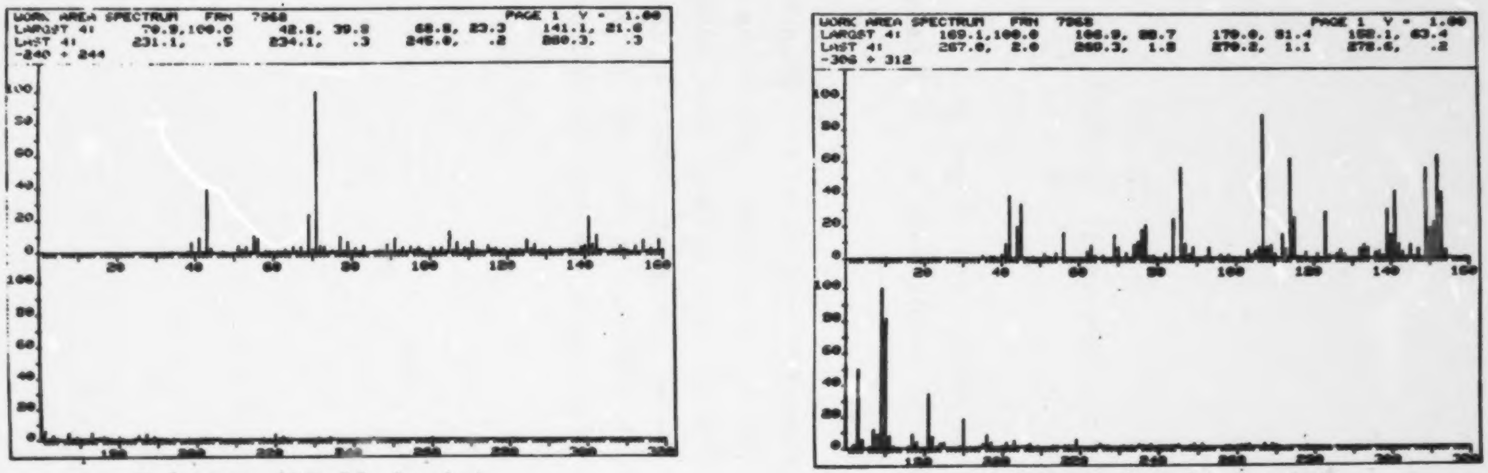
Figure 44. Total ion reconstructed chromatogram of Port Neches downstream water sample #1.

- p-chlorophenol
- unknown (11.2 min)
- diethyl phthalate
- unknown (14.1 min)
- isothazine
- unknown (14.8 min)
- unknown (16.0 min)
- isobutylphthalate
- dioctylphthalate
- 2,7,11-trimethyldodeca-2-trans,6-cis-10-trienol
- triphenylphosphine oxide

Mass spectra for the four unknown compounds are shown in Figure 45. The results for the spiked water sample are listed in Section 7.2.2.

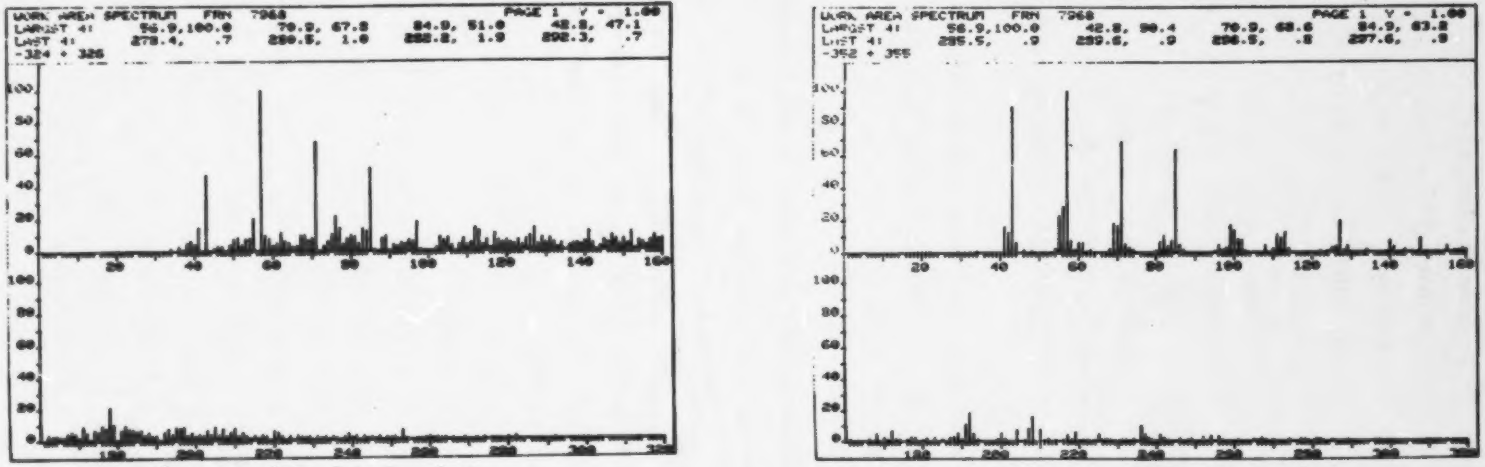
The same water sample (W-1, downstream #1) was also analyzed by GC/MS in the normal scan mode in a Tenax GC column. A series of polar compounds not identified on the SP 2250 column was identifield on the Tenax GC column. The total ion reconstructed chromatogram for the Tenax GC characterization and the identity of the peaks are shown in Figure 46. The compounds identified are listed below.

- phenol
- diethylene glycol monoethyl ether
- α-caprolactone
- p-cresol
- p-chlorophenol
- triethylene glycol
- methyl naphthalene
- acenaphthalene or biphenyl
- unknown (18.9 min)
- nonyl phenol



Unknown (RT=11.2 min)

Unknown (RT=14.1 min)



Unknown (RT=14.8 min)

Unknown (RT=16.0 min)

Figure 45. Mass spectra of unknowns in downstream #1 water sample, Port Neches, Texas.

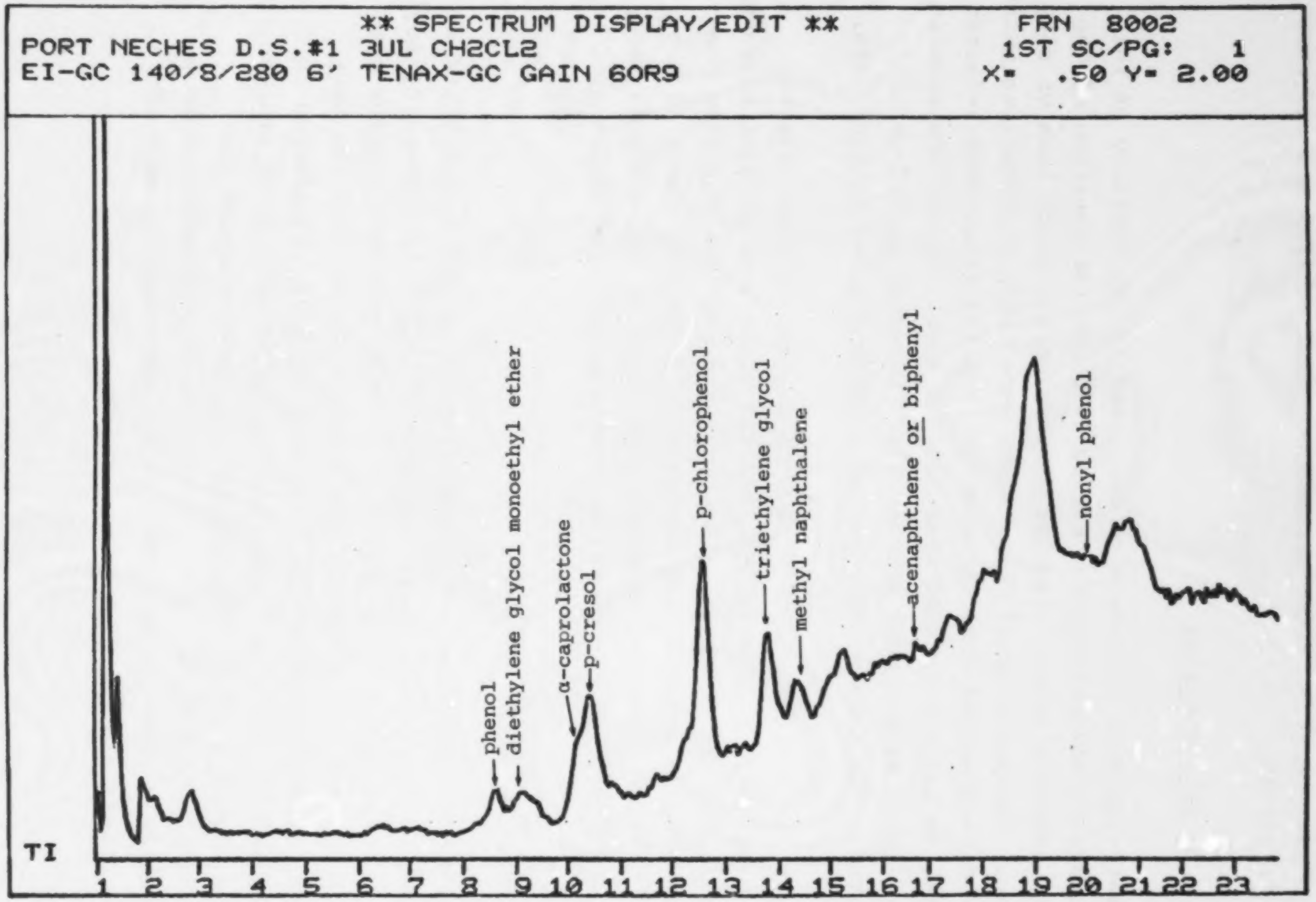


Figure 46. Total ion reconstructed chromatogram of Port Neches, downstream water sample - Tenax GC.

The mass spectrum of the unknown compound at 18.9 min. is shown in Figure 47.

10.2.3 Soil Sampling

Twenty-two soil samples were collected in the vicinity of the Jefferson Chemical Plant. Figure 48 shows the location of the soil sampling sites. Samples were primarily sandy loam or clay loam. The majority of the samples were taken at locations which would be downwind from the plant. Sampling sites were selected based on the annual wind rose for the area. All of the samples were taken with a bulb planter (5 cm diameter by 7.5 cm in depth). The samples were placed in wide mouthed canning jars.

After air freight shipment back to Dayton, 50 g of selected samples (S-2, S-3, S-4, S-5, S-7 and S-13) were soxhlet extracted with methylene chloride. The methylene chloride was then concentrated to ∿ 2.5 ml and analyzed by GC/MS/SIM. None of the six β-chloroethers of interest were found in the six soil samples. Detection limits for the β-chloroethers were 4×10^{-9} g/g of soil.

10.2.4 Sediment Sampling

A sediment sample was collected at each of the downstream water sampling locations. Figure 49 shows the sediment sampling sites on a topographical map of the area. The sediment samples were scooped from the bottom of the creeks ∿ 0.5 m from the bank with a collapsible shovel. The samples were transferred to wide mouthed canning jars. After Soxhlet extraction and concentrations to ∿ 2.5 ml, the samples were analyzed via GC/MS/SIM. None of the six β-chloroethers of interest were detected in the two samples. Detection limit for each of the ethers was 4×10^{-9} g/g of sediment.

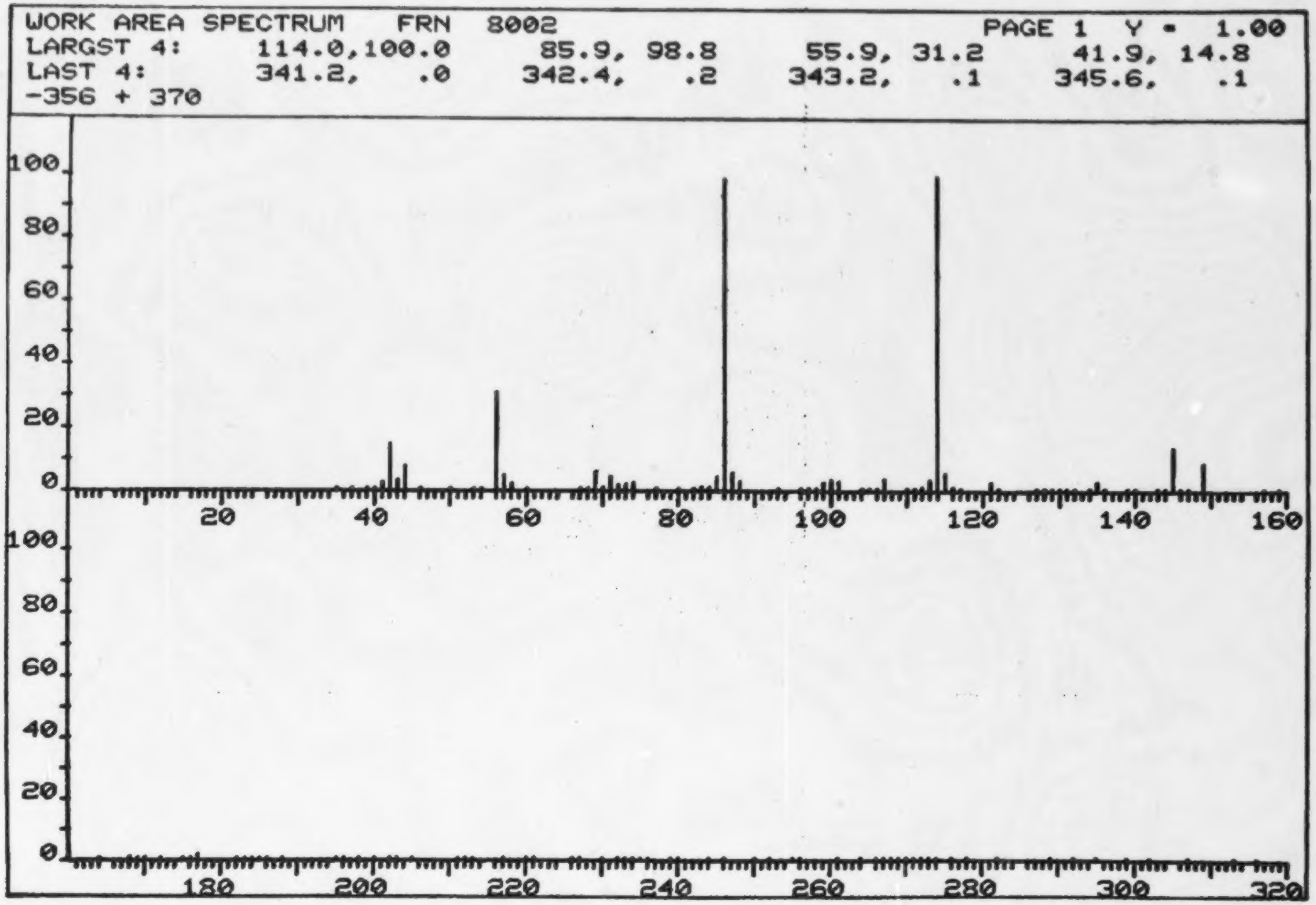


Figure 47. Unknown (RT=18.9 min) (see Figure 46).

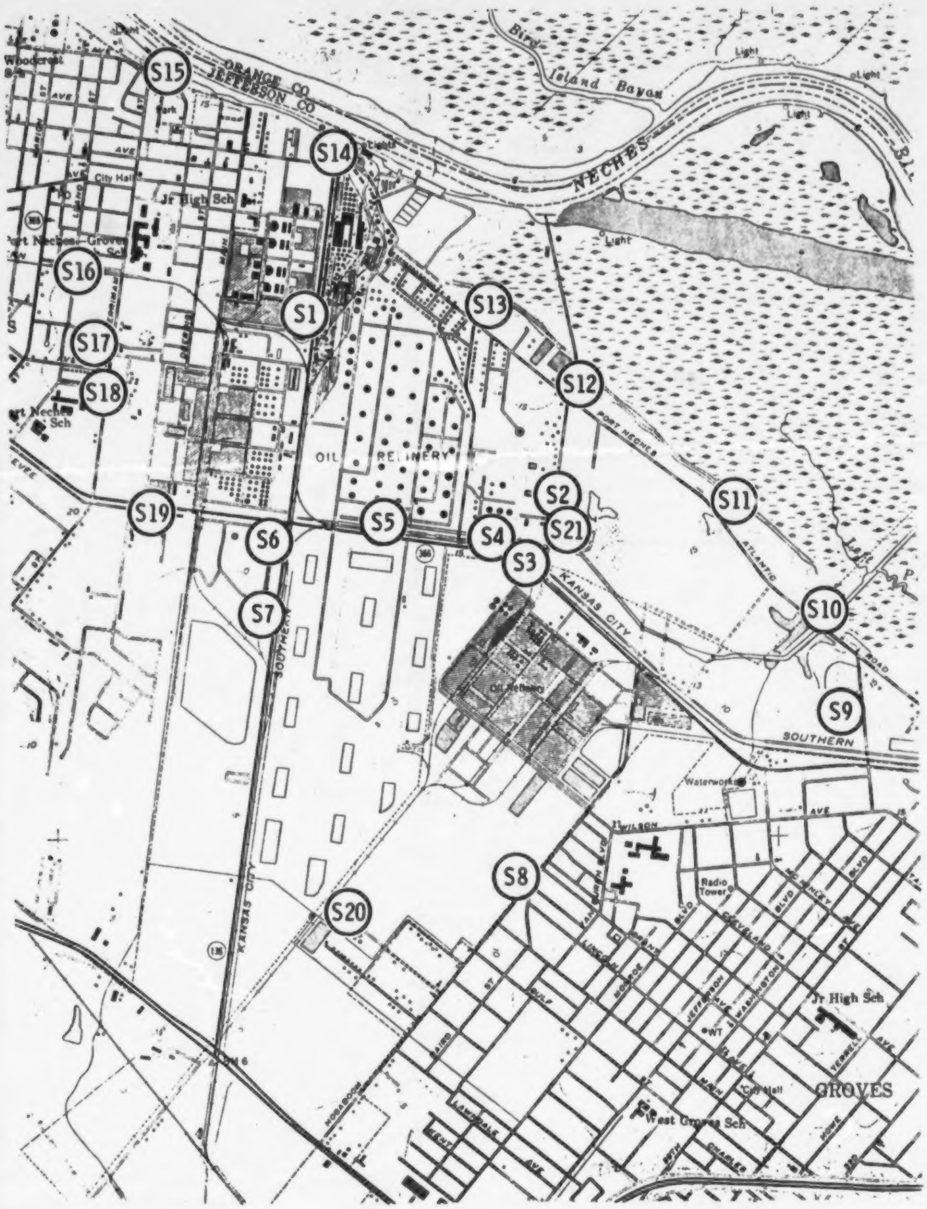

S1
S2
S3
S4
S5
S6
S7
S8
S9
S10
S11
S12
S13
S14
S15
S16
S17
S18
S19
S20
S21
ORANGE CO
JEFFERSON CO
NECHES
Bird Island Bayou
OIL REFINERY
Jr High Sch
City Hall
Port Neches-Groves Sch
KANSAS CITY
SOUTHERN
ATLANTIC
Waterworks
Radio Tower
Jr High Sch
GROVES
West Groves Sch

Figure 48. Soil sampling sites at Jefferson Chemical, Port Neches, Texas.

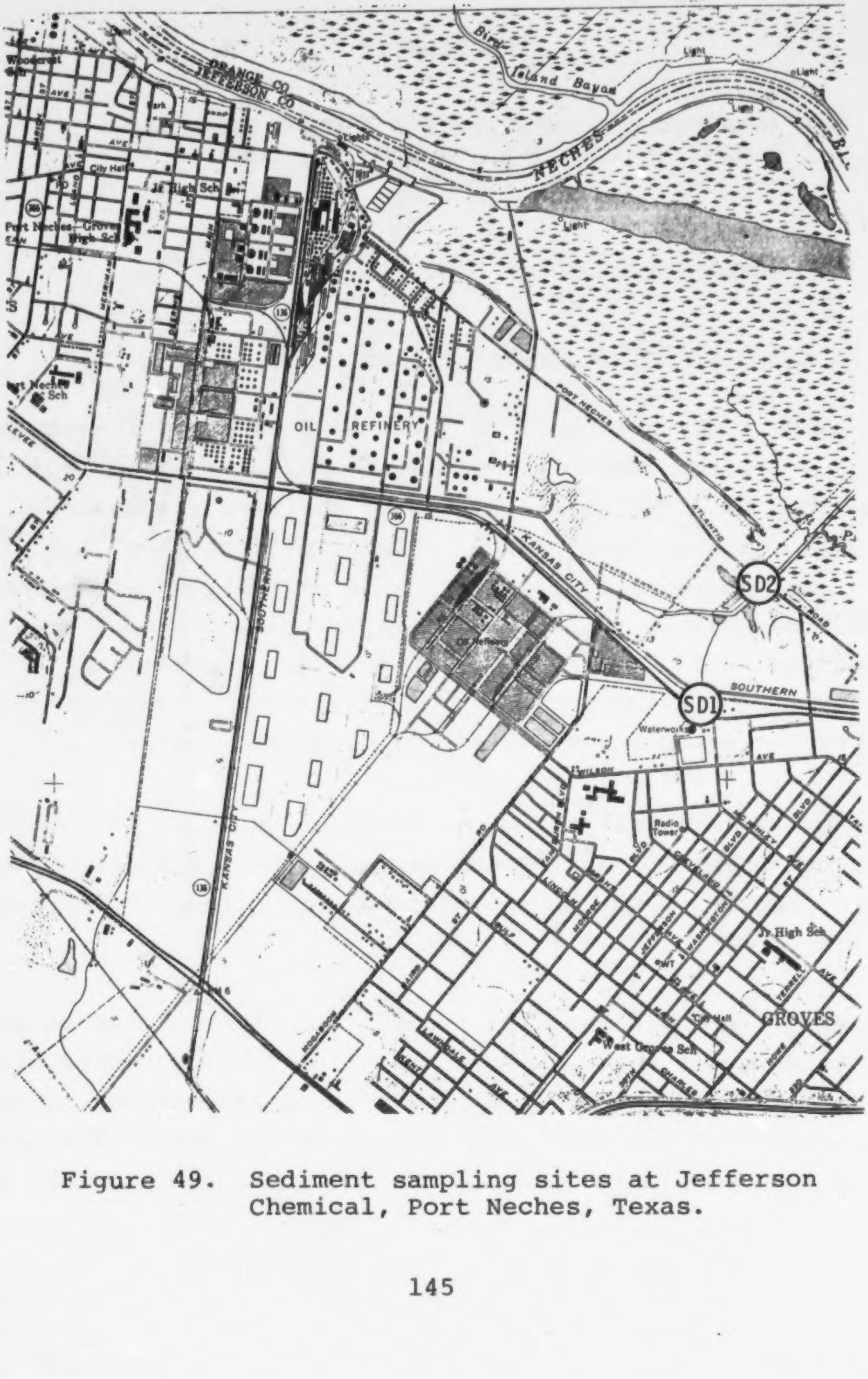

ORANGE CO
JEFFERSON CO
Bird Island Bayou
NECHES
Light
Woodcrest Sch
City Hall
Jr High Sch
Port Neches-Groves High Sch
Port Neches Sch
LEVEE
OIL REFINERY
Oil Refinery
PORT NECHES
ATLANTIC
KANSAS CITY
SOUTHERN
SD2
SD1
Waterworks
WILSON AVE
Radio Tower
Jr High Sch
City Hall
West Groves Sch
GROVES

Figure 49. Sediment sampling sites at Jefferson Chemical, Port Neches, Texas.

SECTION 11

SAMPLING AND ANALYSIS FOR β-CLOROETHERS AT DOW CHEMICAL USA, PLAQUEMINE, LOUISIANA

11.1 PRESAMPLING SURVEY

11.1.1 Description of the Plant Site

Dow Chemical USA is located on River Road north of Plaquemine, Louisiana 70764. The plant's mailing address is P.O. Box 150, Plaquemine, LA. The plant produces a variety of industrial organic chemicals. Among the products produced at this plant are ethylene oxide (production capacity = 2.04×10^8 kg/yr) and propylene oxide (production capacity = 1.54×10^8 kg/yr). As has been mentioned earlier the respective by-products of these two chemicals where they are produced by the chlorohydrin process are bis(2-chloroethyl) ether and bis(2-chloroisopropyl) ether.

A presurvey of the plant was performed on June 26, 1977. The presurvey consisted of visual inspection of the Dow Chemical complex, since contact with plant personnel was not allowed, and selection of sites for air and water sampling.

The Dow complex at Plaquemine is a series of buildings of open and closed construction, distillation and cooling towers, flares and liquid storage tanks. The location of the complex is shown in Figure 50 on the topographical map of the area. The main portion of the Dow plant is located in an area roughly 1.5 km by

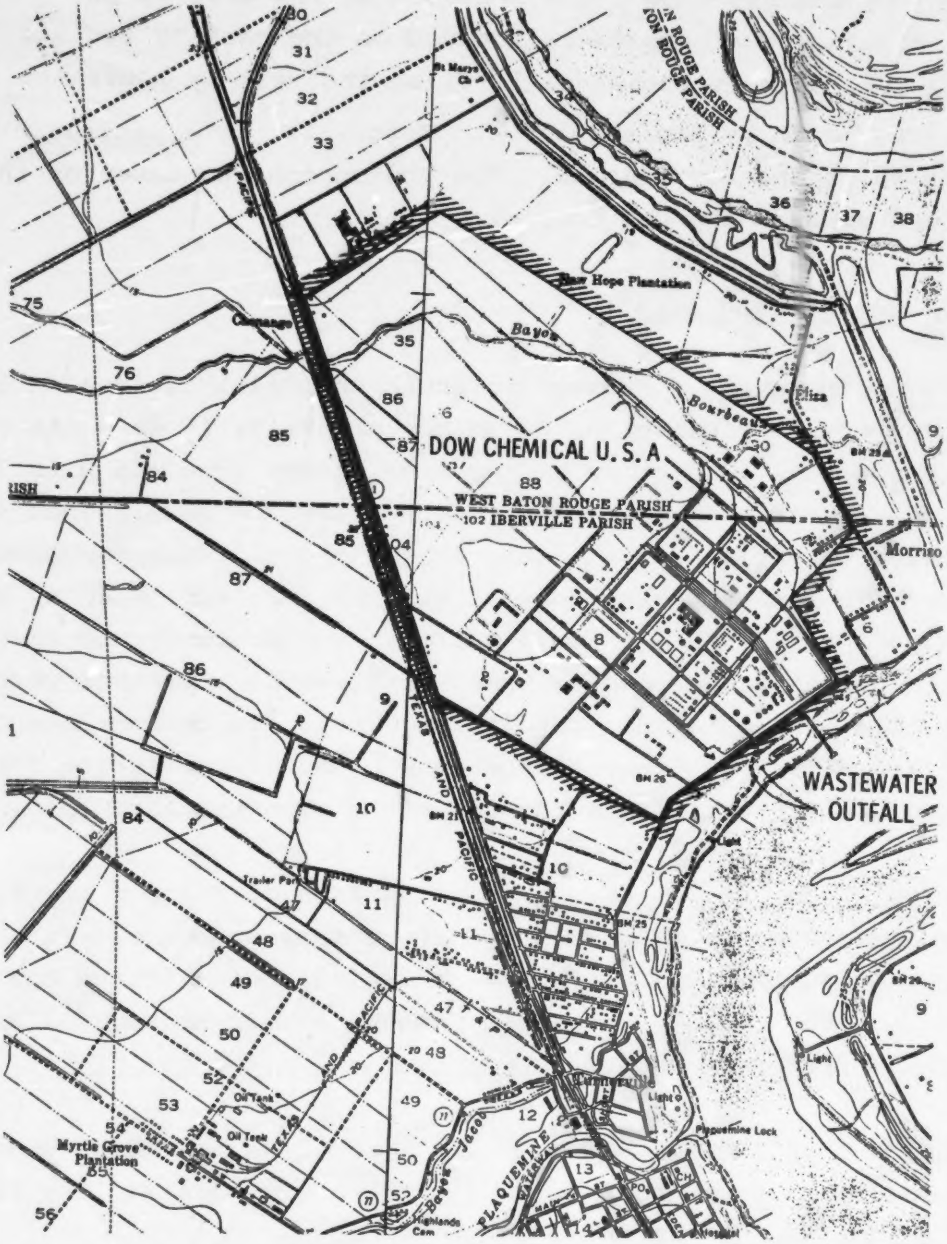

DOW CHEMICAL U. S. A
WASTEWATER OUTFALL
WEST BATON ROUGE PARISH
IBERVILLE PARISH
New Hope Plantation
Bayou
Bourbeaux
Myrtle Grove Plantation
Oil Tank
Trailer Park
Plaquemine Lock
PLAQUEMINE
Morriso

Figure 50. Dow Chemical location in Plaquemine, La. area.

2.5 km. The entire area owned by Dow encompasses ~2.5 km by 3.0 km. Figure 51 show the dimensions of the area on the topographical map. The complex is bounded on the east by Louisiana 988, on the south by Louisiana 1148, on the west by Louisiana 1 and on the north by Louisiana 990. Figure 52 is a panoramic photograph of the Dow complex. The photograph was taken on the southwest side of the Dow complex.

11.1.2 Surrounding Area

The Plaquemine area is located in south central Louisiana on the west bank of the Mississippi River approximately 16 km south of Baton Rouge, La. Elevation of the area ranges from 4.5 m to 7.5 m above sea level. The area is protected from the Mississippi River by a levee which is ~7.3 m high. The majority of the Dow plant proper is in Iberville Parish with part of the land owned by Dow extending into West Baton Rouge Parish. Due south of the Dow complex is a small settlement named Turnerville. Further south is the town of Plaquemine (population 7700). To the northwest of the plant is a small settlement named Addis (population 700). The remainder of the area surrounding the plant is farm land.

Industry in the area other than Dow consists of a small plant run by Copolymer Rubber and Chemical Corporation, a Goodyear Tire and Rubber Co. plant which adjoins Dow on the east side of the Dow complex and Sid Richardson Carbon Company on Sid Richardson Road northwest of the Dow complex.

Vegetation in the area includes locust, cypress and other deciduous trees and a number of varieties of small bushy plants. The farm land in the area had recently been plowed.

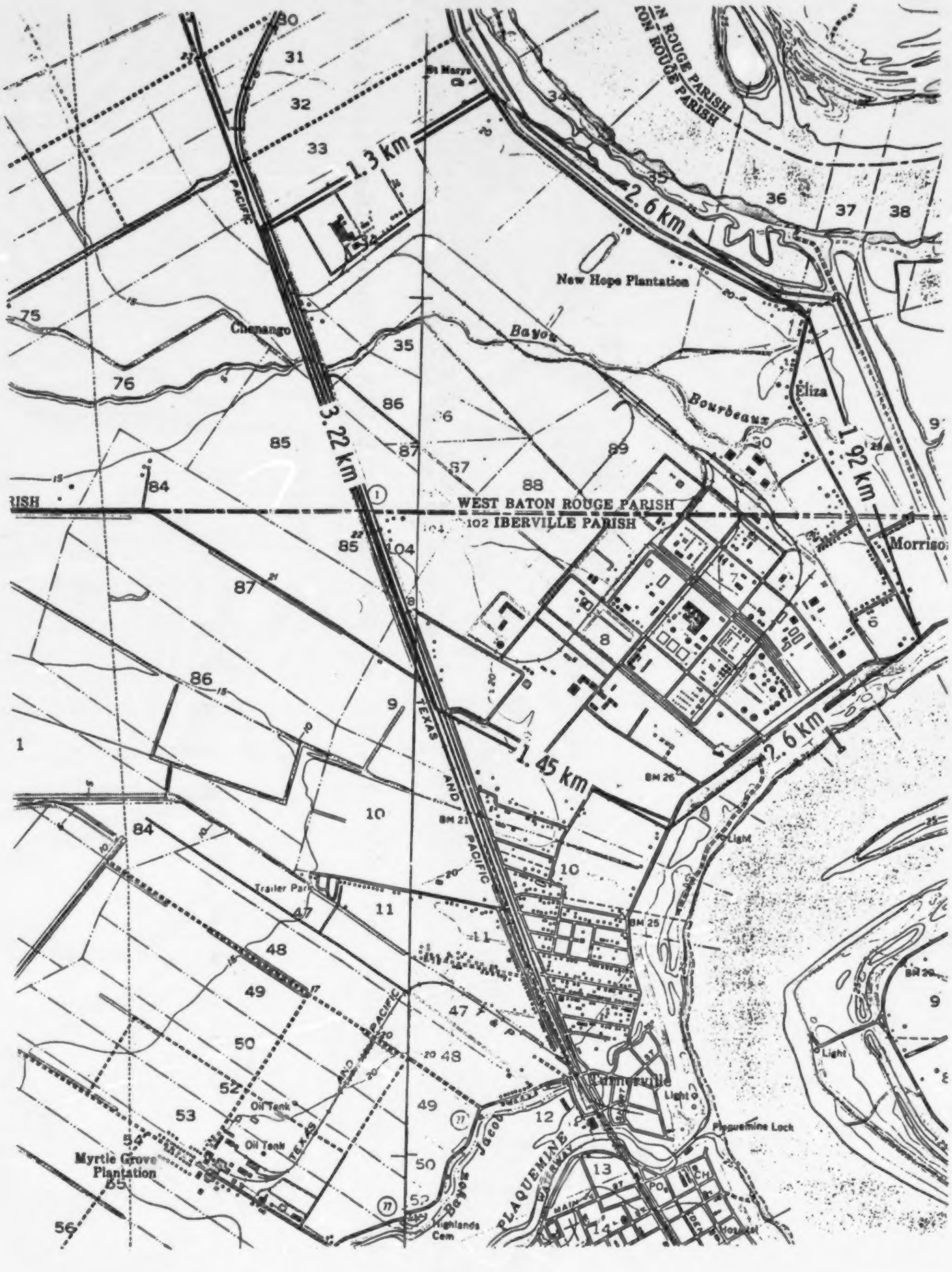

1.3 km
2.6 km
3.22 km
1.92 km
1.45 km
2.6 km
WEST BATON ROUGE PARISH
IBERVILLE PARISH
New Hope Plantation
Chenango
Bayou
Bourbeaux
Eliza
Morrison
St Marys Ch
Trailer Park
Oil Tank
Oil Tank
Myrtle Grove Plantation
Plaquemine Lock
Light
Highlands Cem
PLAQUEMINE
TEXAS AND PACIFIC
PACIFIC
Bayou Jacob

Figure 51. Dimension of area around Dow Chemical USA, Plaquemine, Louisiana.

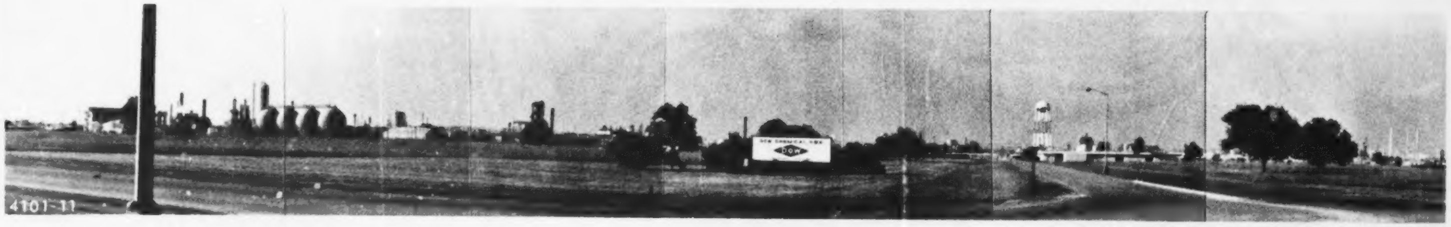


Figure 52. Composite panoramic photograph of Dow Chemical USA, Plaquemine, Louisiana.

11.2 SAMPLING AND ANALYSIS RESULTS

Sampling of the area around Dow Chemical, Plaquemine, Louisiana for β-chloroethers was conducted on 27-28 June 1977. The conditions, locations and results for air, water, soil and sediment samples collected during this sampling are contained in the following subsections.

11.2.1 Air Samples

The deployment of the air samplers around the Dow complex is shown on the topographical map in Figure 53. A total of eight samplers of the personnel sampler type were used for sampling at this site. A description of the samplers, the large Tenax tubes used to collect the β-chloroethers and the charcoal backup tubes is included in Section 4.1. Table 39 describes the sample numbers, Tenax tube number, a description of the sampling location, the compass reading for the sampling sites relative to the center by the Dow plant, the starting and ending sampling times, duration of sampling, the volume of air sampled and β-chloroether(s) detected. Because of the predominant wind direction (S-SW) during sampling, samples A-2, A-3 and A-4 were background samples. Samples A-1, A-5, A-6, A-7 and A-8 formed an arc around the downwind side of the complex. Sample A-9 was the background sample for A-10 when these samples were collected during the night of June 27-28, 1977. Table 40 lists the wind speed and direction data for the sampling periods listed in Table 39. Data in Table 40 were recorded by the weather bureau at Ryan Airport, Baton Rouge,

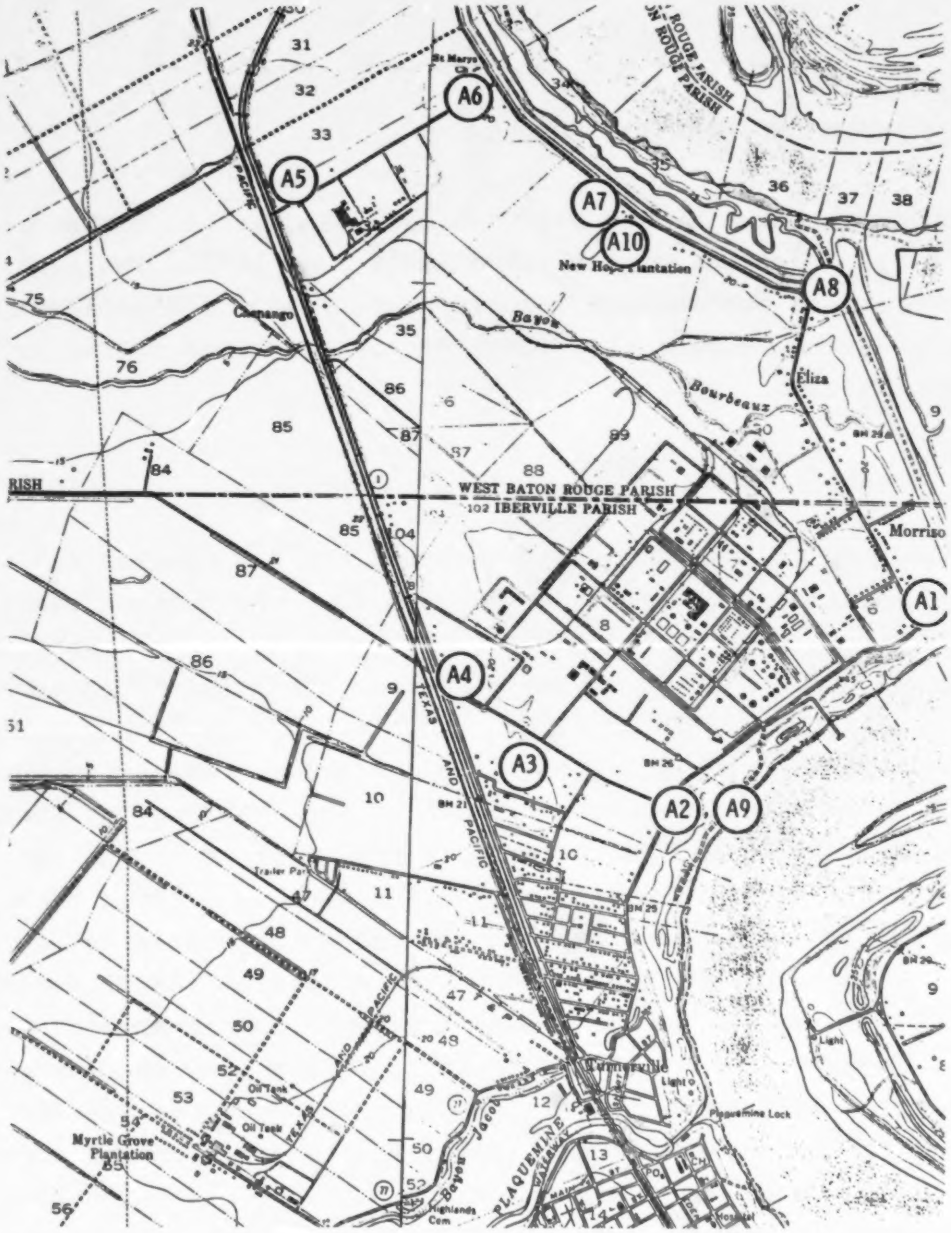

A1
A2
A3
A4
A5
A6
A7
A8
A9
A10
St Marys
New Hope Plantation
Bayou
Bourbeaux
Eliza
Morriso
WEST BATON ROUGE PARISH
IBERVILLE PARISH
TEXAS AND PACIFIC
Trailer Park
Oil Tank
Myrtle Grove Plantation
Plaquemine Lock
Bayou Jacob
PLAQUEMINE
Light
Highlands Cem

Figure 53. Air sampler location at Dow Chemical USA, Plaquemine, Louisiana.

TABLE 39. AIR SAMPLING AT DOW CHEMICAL USA, PLAQUEMINE, LA. 27-28 JUNE 1977

Sample (Tenax Tube)	Location	Compass reading	Sampling				β-Chloroether(s) detected
			Start time	End time	Duration, min.	Volume, l	
A1 (G-45)	NE Side of LA 988, 1.6 km N of LA 1148	80	0945 (6-27)	1800 (6-27)	495	495	None
A2 (G-51)	E Side of LA 988 at intersection with LA 1148	170	1000 (6-27)	1811 (6-27)	491	491	None
A3 (G-50)	SW Side of LA 1148, 0.32 km NW of Brownie St.	185	1010 (6-27)	1822 (6-27)	492	492	None
A4 (G-44)	NE Corner of intersection of LA 1148 and LA 1	225	1017 (6-27)	1828 (6-27)	491	491	None
A5 (G-46)	NE Corner of intersection of LA 990 and LA 1	320	1040 (6-27)	1834 (6-27)	474	474	None
A6 (G-15)	S Corner of intersection of LA 990 and LA 988	355	1048 (6-27)	1848 (6-27)	480	480	None
A7 (G-49)	S Side of LA 988, 0.81 km SE of LA 990	360	1055 (6-27)	1855 (6-27)	480	480	None
A8 (G-48)	E Side of LA 988, 2.6 km SE of LA 990	55	1103 (6-27)	1903 (6-27)	480	480	None
A9 (G-47)	E Side of LA 988 at intersection with LA 1148	170	1820 (6-27)	0951 (6-28)	931	931	None
A10 (G-20)	S Side of LA 998, 0.81 km SE of LA 990	360	1857 (6-27)	1010 (6-28)	913	913	None
A11 (G-43)	SPIKED - 100 μl of Standard	-	-	-	-	-	See Section 7.2.1
A12 (G-19)	CONTROL	-	-	-	-	-	See Section 7.2.1

TABLE 40. WEATHER CONDITIONS DURING SAMPLING AT DOW CHEMICAL USA, PLAQUEMINE, LOUISIANA 22-35°C

	Wind	
Time (Date)	Speed, km/hr	Direction, degrees
June 27, 1977		
0853	16.7	230
0955	13.0	200
1053	20.4	200
1153	18.5	200
1251	22.4	230
1354	18.5	230
1456	25.9	210
1552	31.5	240
1652	18.5	220
1752	22.4	190
1852	20.4	230
1952	18.5	230
2052	16.7	220
2152	18.5	200
2252	9.3	190
2353	11.1	190
June 28, 1977		
0056	0	-
0157	0	-
0257	0	-
0358	0	-
0451	0	-
0529	0	-
0656	0	-
0755	5.6	260
0854	5.6	220
0951	14.8	230
1053	13.0	210

La. The temperature during sampling ranged from 22°C at night to 35°C during the day. The weather was good during the entire sampling period with no rain occurring.

Air samples A-1 through A-7 and A-9 and A-10 were solvent desorbed with methanol as described in Section 5.1. Four cm^3 of methanol was used for each desorption. The desorbed samples were analyzed by gas chromatography/mass spectrometry. The mass spectrometer was operated in the selected ion monitoring mode. None of the six β-chloroethers of interest were detected in these samples (average detection limit = 7×10^{-7} g/m^3). The average detection limit for the two samples collected during the night was 3.9×10^{-7} g/m^3. One of the air samples, A-8, was thermally desorbed and analyzed by GC/MS. The mass spectrometer was operating in the scanned mode. None of the β-chloroethers of interest were detected in this sample (average detection limit $\sim 2 \times 10^{-7}$ g/m^3). The total ion reconstructed chromatogram is shown in Figure 54. The identity of peaks seen in the chromatogram are also listed on Figure 54. The compounds found in sample A-8 were:

- methylene chloride
- 2,2,3,3-tetramethyl butane
- benzene
- toluene
- chlorobenzene

Results for the spiked sample are listed in Section 7.2.1.

11.2.2 Water Samples

Original plans for the water sampling at Dow Chemical, Plaquemine, La. called for three 24-hr integrated water samples. However, during sampling the period the downstream #2 water sampler disappeared. Therefore, upstream (W-3) and downstream #1 (W-1) water samples were 24-hr composite samples and downstream #2 (W-2) was

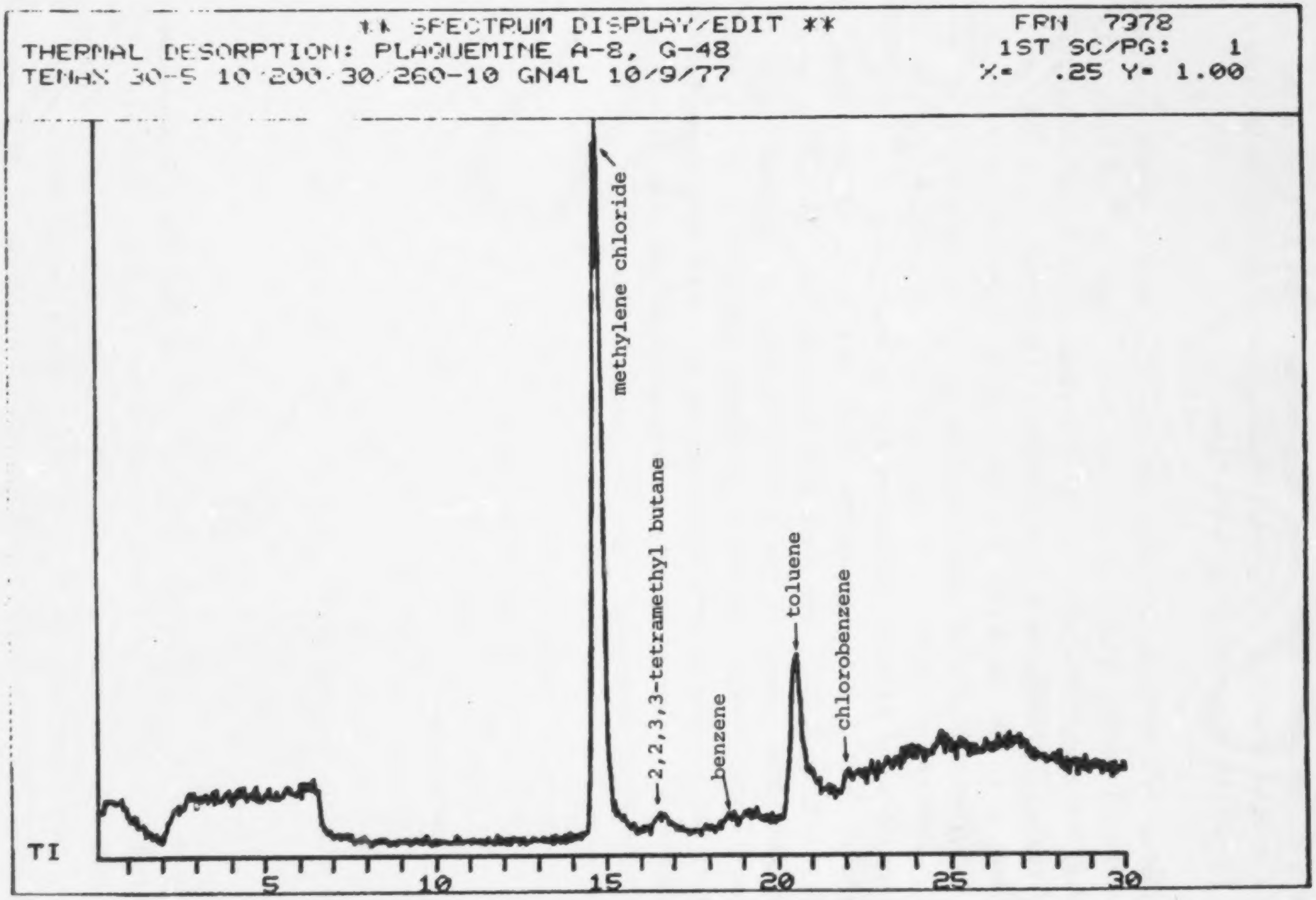


Figure 54. Total ion reconstructed chromatogram of air sample A-8, thermally desorbed, Dow Chemical USA, Plaquemine, Louisiana.

a grab sample. The locations of the water samples are shown on the topographical map of the area in Figure 55. Table 41 lists the sample numbers, sampling location, sampling times, duration and volume, and β-chloroethers detected. The upstream location was ∿1.45 km northeast of the plant wastewater outfall. The downstream #1 location was 0.8 km south of the outfall and the downstream #2 location was ∿2.6 km south of the outfall. The Mississippi River ranged from 0.5 km wide at the downstream #2 location to 1.0 km wide at the upstream location. Photographs of the drainage ditch to the outfall, downstream #1, downstream #2 and upstream locations are shown in Figure 56. Caps of the water sample bottles were taped to insure against leakage. The samples were placed in picnic coolers with foam padding and ice. The cooler was then sealed and the samples air freighted to Dayton. Samples were kept at 4°C until analyzed.

One liter of each sample was extracted three times with 100 cm^3 portions of methylene chloride. The extracts for each sample were combined and concentrated to ∿2.5 cm^3. These concentrates were analyzed by GC/MS/SIM. None of the three samples contained β-chloroethers. The average detections limit for water samples were 2.0×10^{-7} g/l. The concentrate of the downstream #2 sample (w-2) was further concentrated to a volume of 0.5 cm^3. This sample was then characterized via GC/MS using an SP 2250 column. Figure 57 shows the total ion reconstructed chromatogram for this sample and the compounds identified in the sample. Compounds found in the sample were:

- 1,2-cyclohexanediol
- unknown (RT = 6.0 min.)
- 5-n-butyl nonane
- 2,6-di-tert-buty-4-methyl phenol
- stilbene
- 2,2-dimethyl-trans-hex-3-ene
- unknown (RT = 15.3 min)

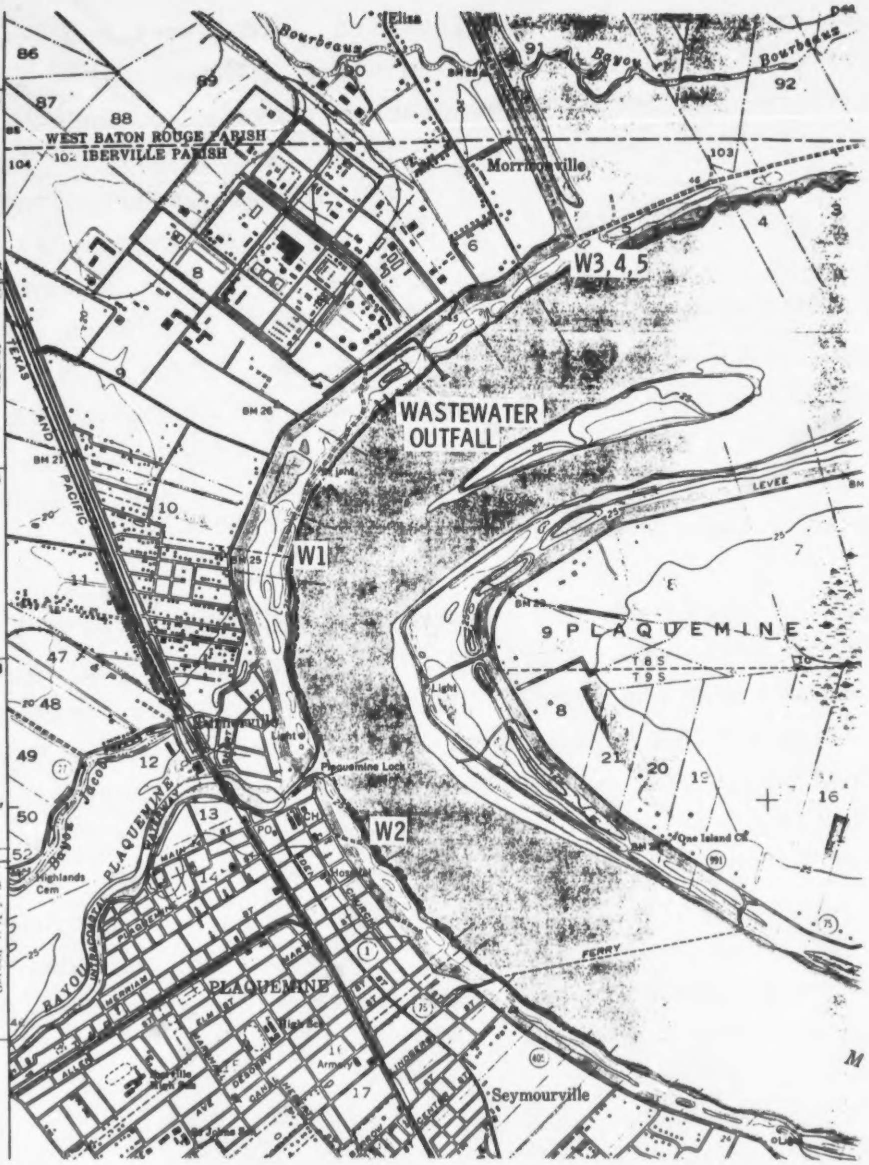
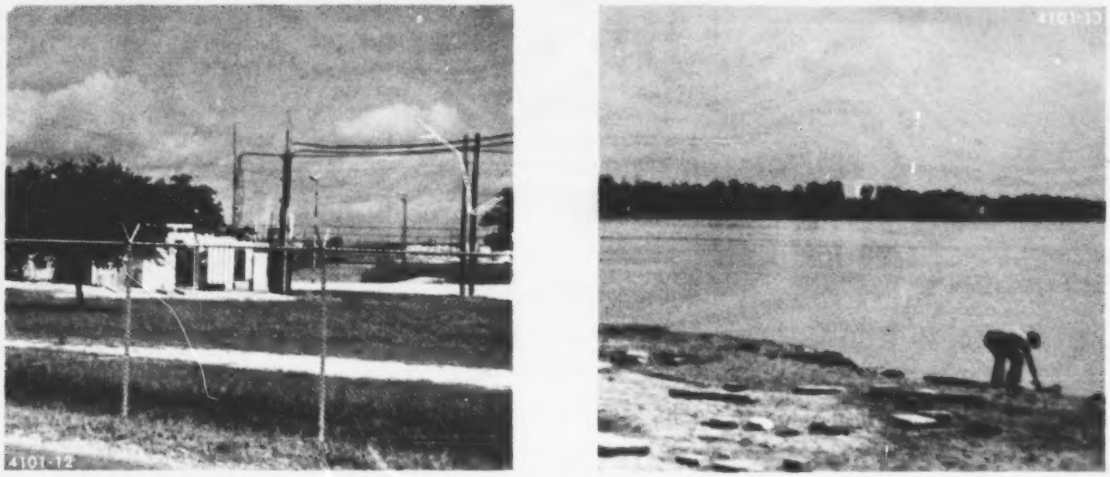

W3,4,5
WASTEWATER OUTFALL
W1
W2
WEST BATON ROUGE PARISH
IBERVILLE PARISH
Morrisonville
PLAQUEMINE
Plaquemine Lock
Seymourville
Bayou Bourbeaux
LEVEE
FERRY
TEXAS AND PACIFIC
Highlands Cem

Figure 55. Water sampler location at Dow Chemical USA, Plaquemine, La.

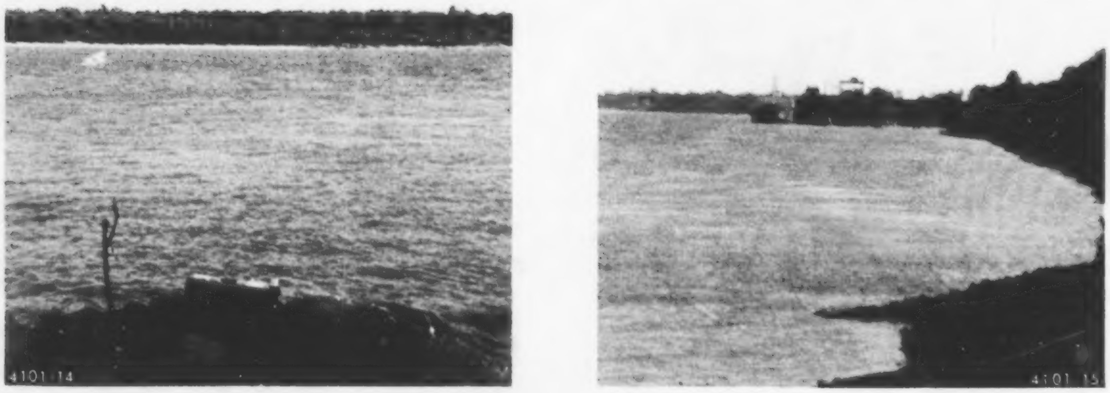
TABLE 41. WATER SAMPLING AT DOW CHEMICAL USA PLAQUEMINE, LA. ON 27-28 JUNE 1977

Sample	Location	Sampling				β-Chloroether(s)
		Start time	End time	Duration, min	Volume, ℓ	
W-1	W bank of Mississippi R. 800 M S of Dow Waste Water Outfall	0845 (6-27)	0845 (6-28)	1440	4	None
W-2	W bank of Mississippi R. 10 M N of intersection with Court St in Plaquemine, LA.	0920 (6-27)	Grab Sample 0920 (6-28)	-	4	None
W-3	W bank of Mississippi R. 10 M S of intersection with Davis St, E of LA 988	0930 (6-37)	0930 (6-28)	1440	4	None
W-4	Same as W-3	Grab 0930 (6-28)	-	-	1	See Section 7.2.1
W-5	Same as W-3	Grab 0930 (6-28)	-	-	1	See Section 7.2.1


4101-12
4101-13

a. Drainage ditch

b. Downstream #1


4101-14
4101-15

c. Downstream #2

d. Upstream

Figure 56. Photographs of drainage ditch and water sampling locations, Dow Chemical USA, Plaquemine, Louisiana.

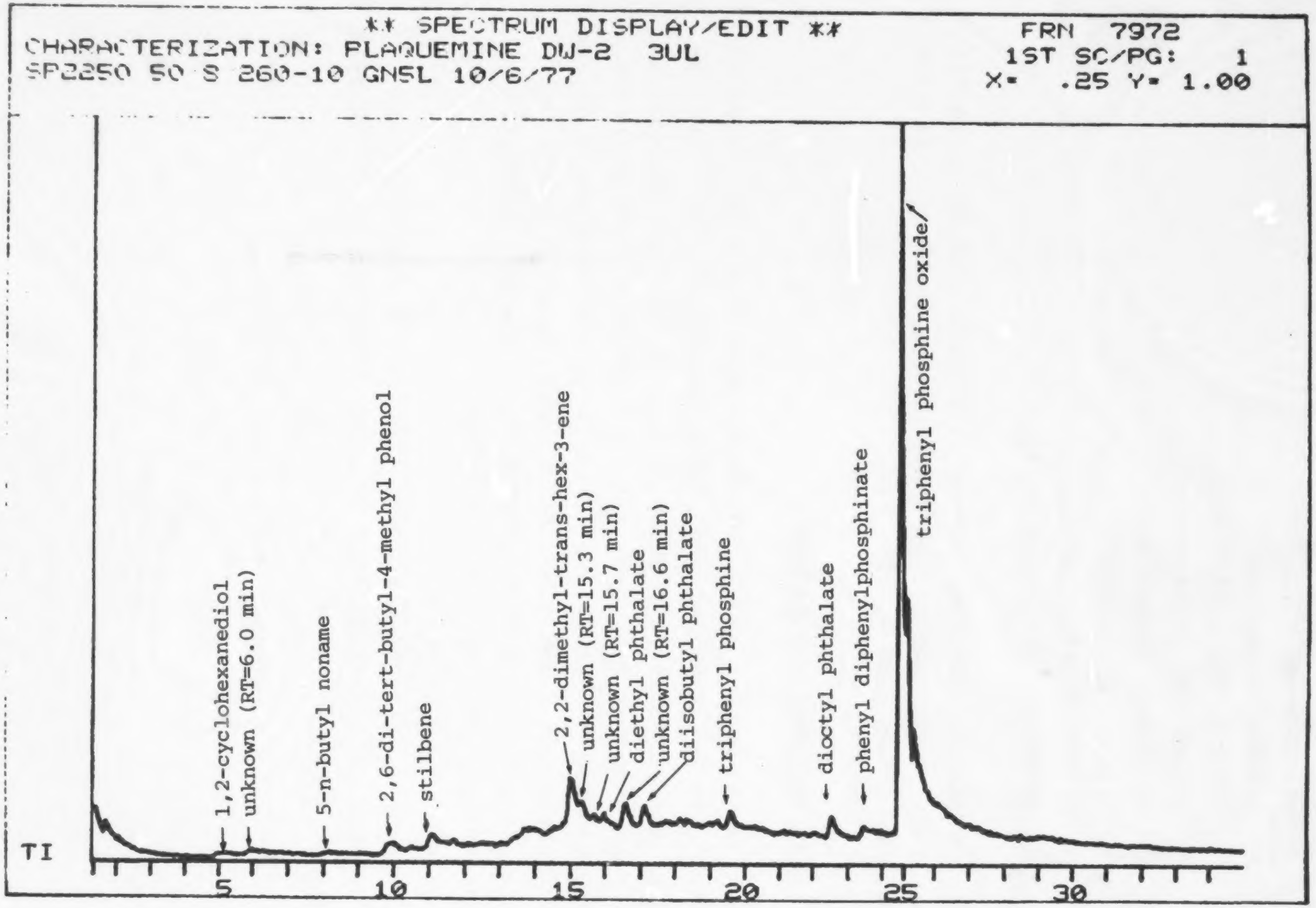


Figure 57. Total ion reconstructed chromatogram for downstream #2 water sample (W-2), Dow Chemical USA, Plaquemine, La.

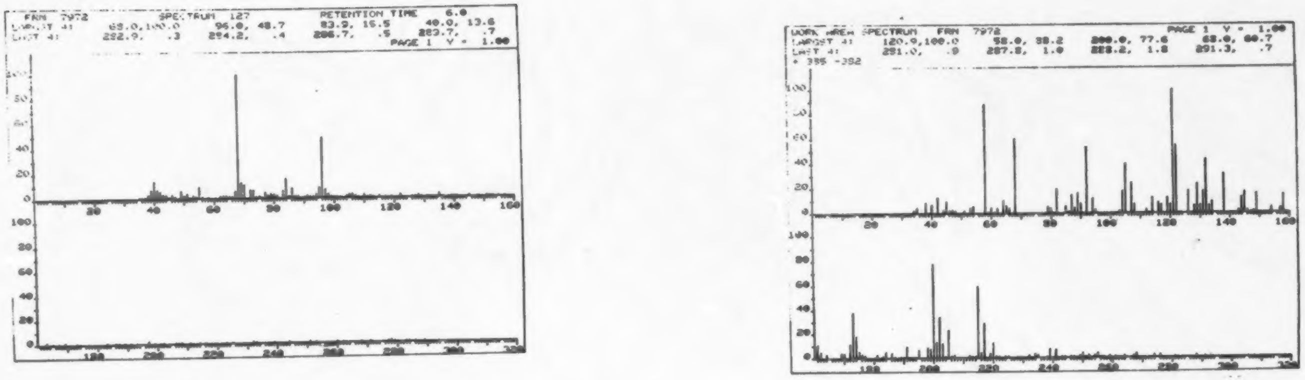
- unknown (RT = 15.7 min)
- diethyl phthalate
- unknown (RT = 16.6 min)
- diisobutyl phthalate
- triphenyl phosphine
- dioctyl phthalate
- phenyl diphenyl phosphinate
- triphenyl phosphine oxide

The mass spectra for the four unknown compounds are shown in Figure 58. Results for the spiked water sample (W-5) at this site are described in Section 7.2.2.

11.2.3 Soil and Sediment Samples

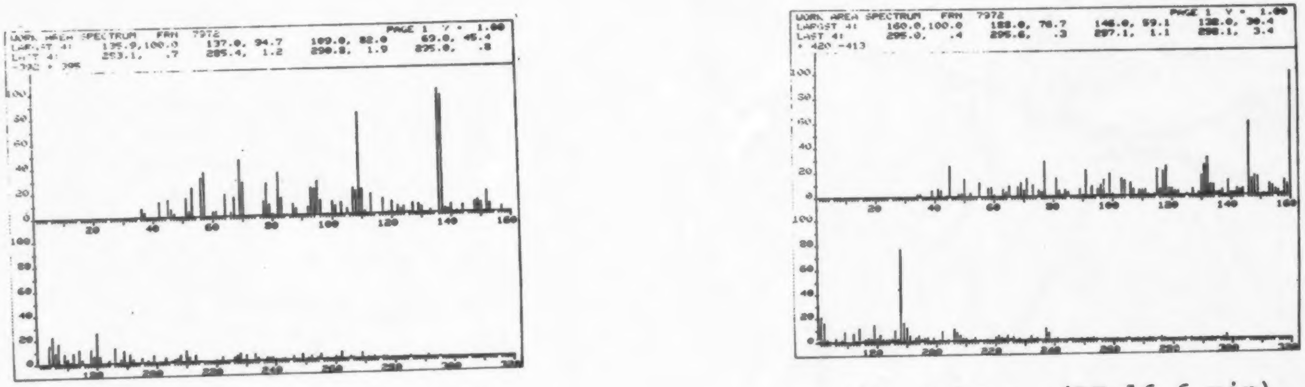
A total 15 soil samples and 2 sediment samples were collected in the area of the Dow Chemical USA plant, Plaquemine, La. The locations of these samples are shown in Figure 59. Of the samples taken 5 soil samples, S-6, S-7, S-8, S-9 and S-10, and both sediment samples were analyzed. For details on the sampling procedure used see Sections 4.3 and 4.4. Fifty grams of each sample were Soxhlet extracted with methylene chloride. The extracts were concentrated and analyzed via GC/MS/SIM.

None of the seven soil and sediment samples contained the six β-chloroethers of interest. The average detection limit for soil and sediment samples equaled 4×10^{-9} g/g.



(a) Unknown(RT=6.0 min)

(b) Unknown (RT=15.3 min)



(c) Unknown (RT=15.7 min)

(d) Unknown (RT=16.6 min)

Figure 58. Mass spectra of unknown compounds in downstream #2 water sample, Plaquemine, Louisiana.

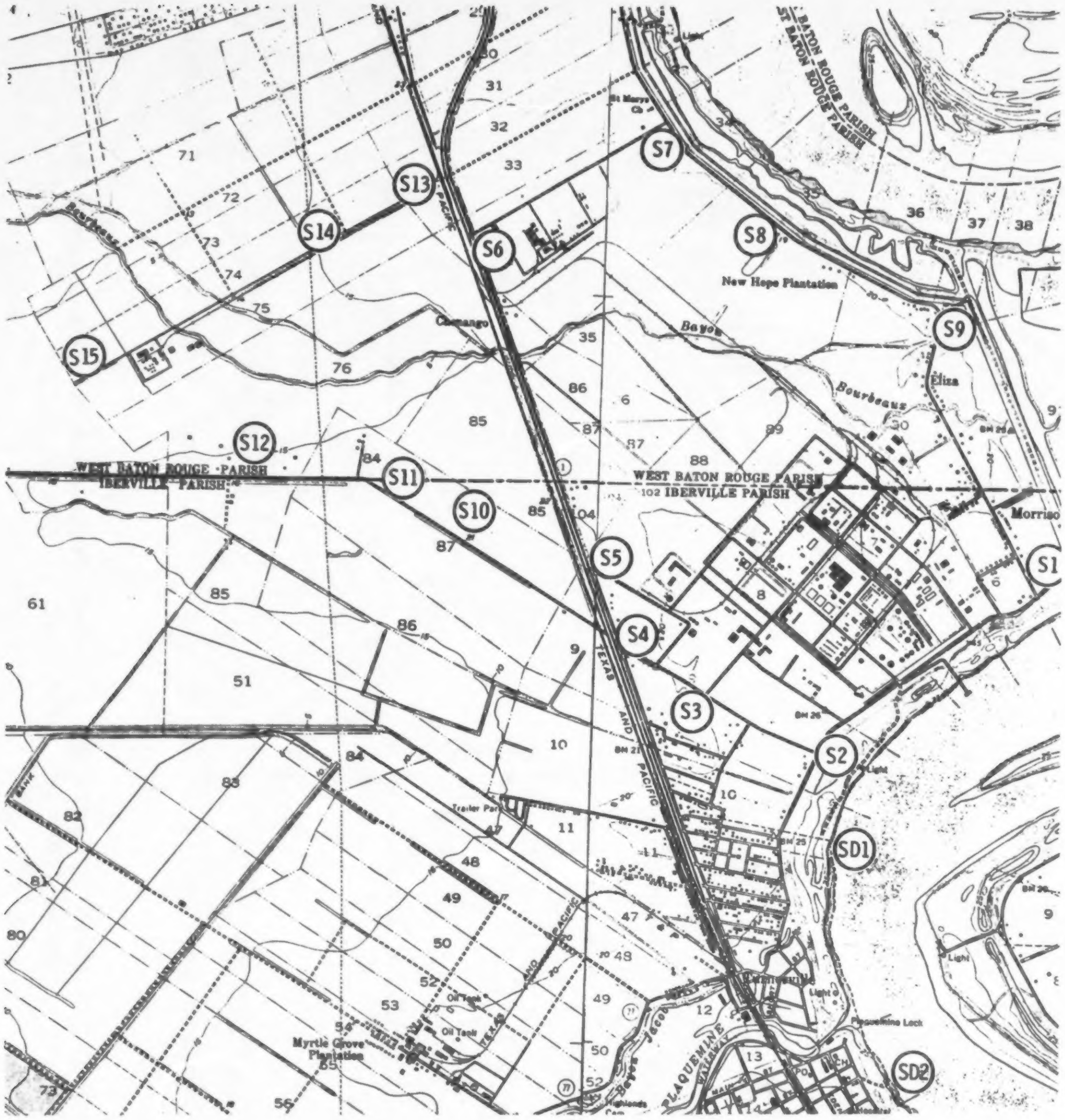

S1
S2
S3
S4
S5
S6
S7
S8
S9
S10
S11
S12
S13
S14
S15
SD1
SD2
WEST BATON ROUGE PARISH
EAST BATON ROUGE PARISH
WEST BATON ROUGE PARISH
IBERVILLE PARISH
New Hope Plantation
Bayou Bourbeaux
Eliza
Morrison
Chenango
TEXAS AND PACIFIC
Trailer Park
Oil Tank
Myrtle Grove Plantation
Bayou Jacob
PLAQUEMINE
Plaquemine Lock
Light

Figure 59. Soil and sediment sampling locations for Dow Chemical USA, Plaquamine, Louisiana.

SECTION 12

SAMPLING AND ANALYSIS FOR β-CHLOROETHERS AT THIOKOL CORPORATION, MOSS POINT, MISSISSIPPI

12.1 PRESAMPLING SURVEY

12.1.1 Description of the Plant Site

Thiokol Corporation is located at 1640 Elder Ferry Road in Moss Point, Mississippi. The plant produces synthetic rubber compounds and chemicals. Among the products they produce are polysulfide rubbers. An intermediate in the production of the polysulfide rubbers is bis(2-chloroethoxy) methane. Bis(2-chloroethoxy) methane is prepared by the condensation of ethylene chlorohydrin with aqueous formaldehyde in the presence of an azeotroping agent. A possible byproduct of the formation bis(2-chloroethoxy) methane is bis(2-chloroethyl) ether. Therefore, two compounds of interest to this research request, which could be present at this site, were bis(2-chloroethoxy) methane and bis(2-chloroethyl) ether.

A presurvey of the Thiokol plant and surrounding area was performed on June 29, 1977. The presurvey consisted of a visual inspection of the plant, since contact with plant personnel was not allowed, and selection of sampling sites for air and water samples.

Figure 60 shows the location of the Thiokol plant site in the Moss Point, Mississippi area topographical map. Also included on the figure are dimensions for the area surrounding the plant. The plant occupies an area ∿ 0.4 km square. The plant is located on the north side of the Escatawpa River. The plant is small by comparison to the other sites described in this report. One major building, some open construction pilot plant type structures, some storage vessels, and a water tower constitute the majority of the plant. Figure 61 is a panoramic photograph of the Thiokol plant site. The photograph was taken from the southwest corner of the Thiokol property.

Wastewater from the plant flows down a concrete-lined drainage ditch under Elder Ferry Road into an open, unlined ditech which flows into the Escatawpa River. Distance from the road to the river is ∿ 0.2 km. The water flowing down the ditch was reddish-brown. A small amount of odor was noticed coming from the plant when standing on the east side of the plant. The plant is served by a spur from the Mississippi Export Railroad. The plant is bounded on the south and east by Elder Ferry Road. To the north and west of the plant are forest areas.

12.1.2 Surround Area

The Moss Point area is on the Mississippi Gulf coastal plain in extreme southeastern Missississippi. Moss Point is ∿ 8 km north of Pascagoula, Mississippi. The elevation of the area ranges from ∿ 3 m to 4.5 m above sea level. Moss Point is located in Jackson County, Mississippi. The population of Moss Point, which is located south across the river from the Thiokol plant, is 19,300. A small community northwest of the plant is named Escatawpa (population 1700). A larger community south of Moss Point is Pascagoula (population 27,300). The area along the Escatawpa River is swampy. A number of types

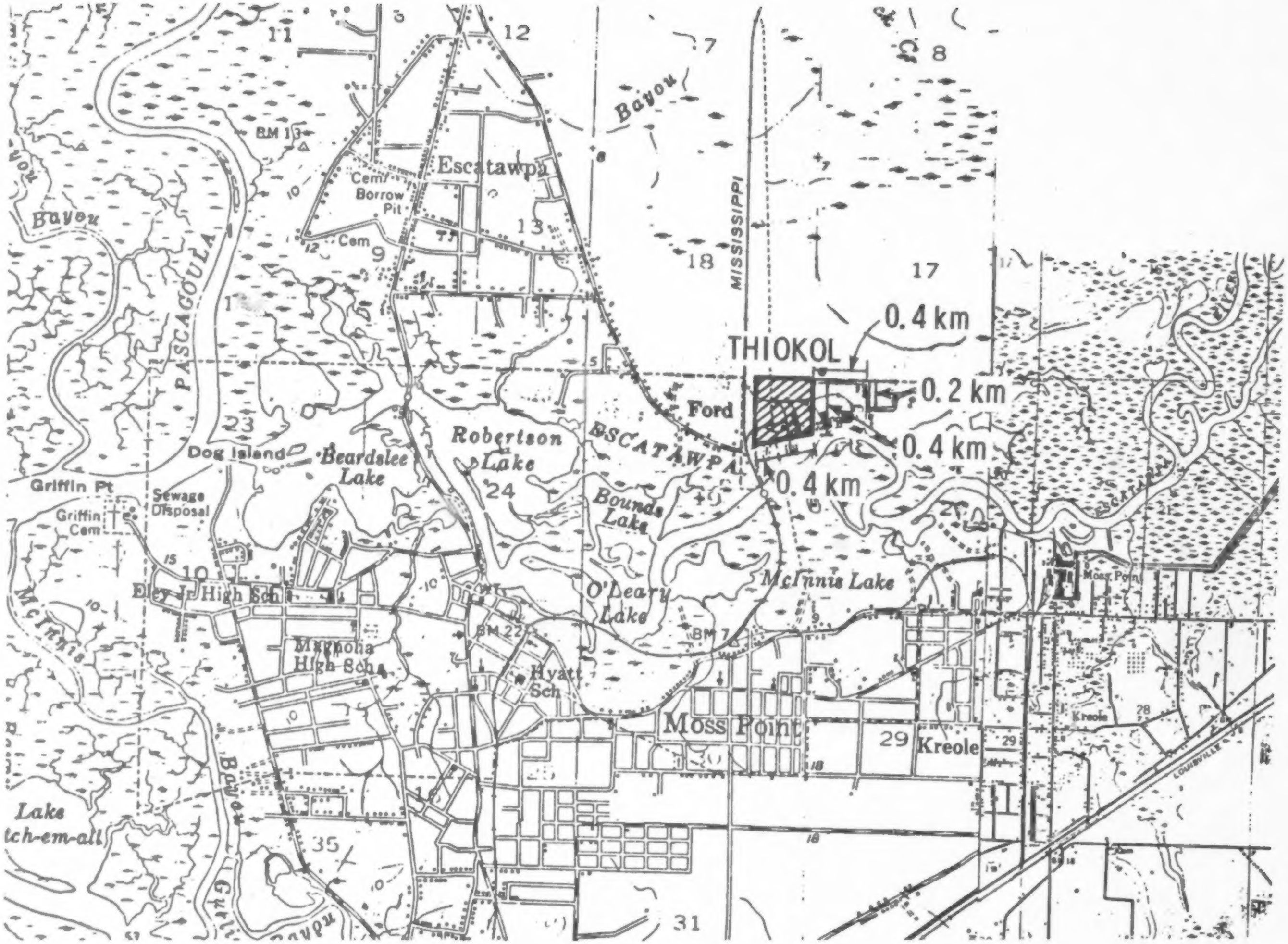

THIOKOL
0.4 km
0.2 km
0.4 km
0.4 km
Ford
ESCATAWPA
MISSISSIPPI
Escatawpa
Moss Point
Kreole
Robertson Lake
Beardslee Lake
Bounds Lake
O'Leary Lake
McInnis Lake
PASCAGOULA
Dog Island
Griffin Pt
Griffin Cem
Sewage Disposal
Cem
Borrow Pit
Bayou
Magnolia High Sch
Hyatt Sch
Eley Jr High Sch
McInnis
Lake
tch-em-all
BM 13
BM 22
BM 7
11
12
7
8
9
13
17
18
23
24
29
31
35

Figure 60. Topographical map of the Moss Point, Mississippi area showing the location of the Thiokol Corporation plant and dimensions of the area around the plant.

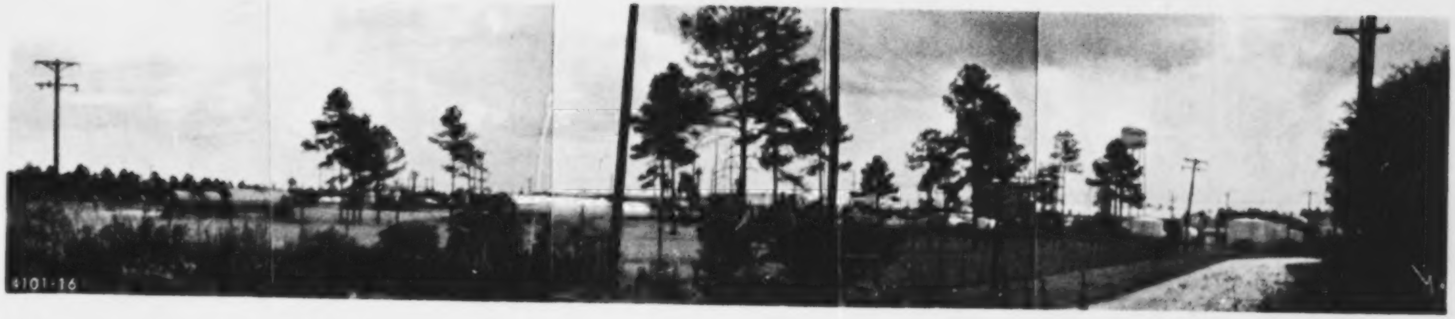


Figure 61. Composite panoramic photograph of Thiokol Corporation, Moss Point, Miss.

of pine trees, deciduous trees and small bushy plants are found in the area. Spanish moss grows from a number of the trees. International Paper Company is located upstream on the Escatawpa River from the Thiokol plant. International manufactures kraft paper and kraft board. Zapata Protein, Inc. and Standard Products, Inc. located east of the Thiokol plant are fish processing plants. A company named Halter Marine is located southwest of the Thiokol plant.

12.2 SAMPLING AND ANALYSIS RESULTS

Sampling of the area around Thiokol Corporation, Moss Point, Mississippi, for β-chloroethers was conducted on June 29-30, 1977. The conditions, locations and results for the air, water, soil and sediment samples collected during this sampling trip are contained in the following subsections.

12.2.1 Air Samples

Seven air samples were deployed around the Thiokol plant on June 29, 1977 for daylight sampling. Three air samplers were used to sample around the plant on the night of June 29-30, 1977. The location of all ten air samplers is shown on the topographical map in Figure 62. A description of the sampling locations, compass readings relative to the center of the Thiokol plant, start and stop times, sampling duration, volume of air sampled and β-chloroethers detected are listed in Table 42.

Sampling was accomplished using portable personnel samplers, large Tenax tubes and charcoal backup tubes described in Section 4.1. Weather conditions were very good during sampling. The temperature ranged from 21°C at night to 35°C during the day. The relative humidity was high, and only one very brief

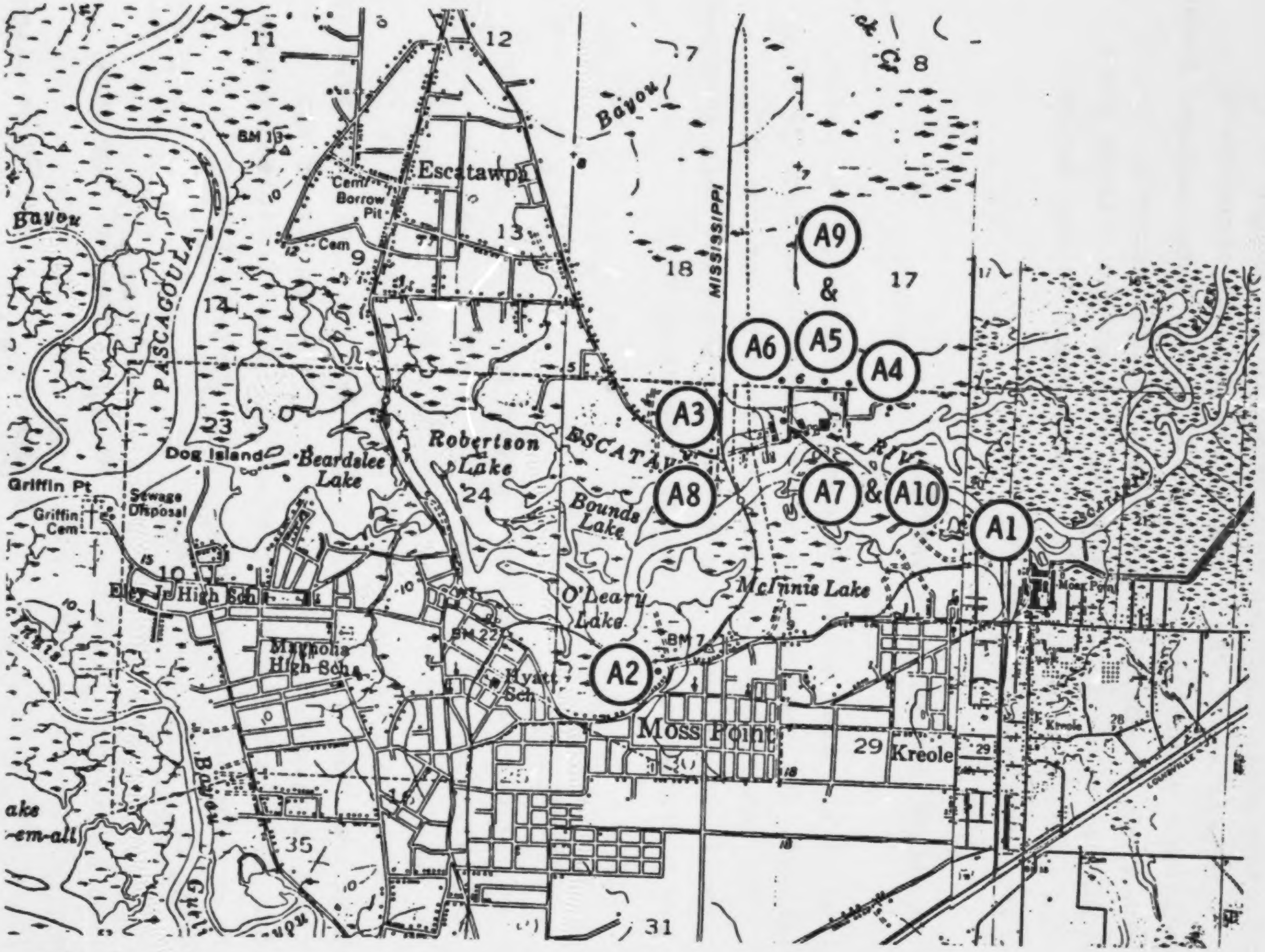

A1
A2
A3
A4
A5
A6
A7
&
A8
A9
&
A10
Escatawpa
Cem
Borrow Pit
Cem
Bayou
PASCAGOULA
Dog Island
Beardslee Lake
Griffin Pt
Griffin Cem
Sewage Disposal
Robertson Lake
Bounds Lake
O'Leary Lake
McInnis Lake
ESCATAWPA RIVER
MISSISSIPPI
Moss Point
Kreole
Hyatt Sch
Magnolia High Sch
Eley Jr High Sch
Bayou
BM 22
BM 7
11
12
7
8
13
9
18
17
14
23
24
10
25
30
29
28
35
31

Figure 62. Location of air samplers at Thiokol Corporation, Moss Point, Mississippi.

TABLE 42. AIR SAMPLING AT THIOKOL CORPORATION, MOSS POINT, MISSISSIPPI ON 29-30 JUNE 1977

Sample (Tenax Tube)	Location	Compass Reading	Sampling				β-chloro-ethers detected
			Start time	End time	Duration, min	Vol., l	
A-1 (G-33)	S Bank of Escatawpa River	115	0914(6-29)	1720(6-29)	486	486	-
A-2 (G-37)	N Side of Elder Road, Moss Point	210	0934(6-29)	1744(6-29)	490	490	-
A-3 (G-39)	S Side of Elder Ferry Rd., W. of Thiokol	245	0953(6-29)	1838(6-29)	525	525	-
A-4 (G-40)	N Side of Elder Ferry Rd. ∿ 0.3 km N.E. of Thiokol	60	1012(6-29)	1856(6-29)	524	524	-
A-5 (G-11)	N Side of Elder Ferry Rd., ∿ 0.2 km N.E. of Thiokol	55	1027(6-29)	1859(6-29)	502	502	-
A-6 (G-22	N Side of Elder Ferry Rd., ∿ 0.1 km N of Thiokol	10	1035(6-29)	1902(6-29)	507	507	-
A-7 (G-8)	W Side of Elder Ferry Rd., ∿ 33 m E of Thiokol	10	1040(6-29)	1905(6-29)	505	505	BCEXM
A-8 (LM-3)	S Side of Elder Ferry Rd., W of Thiokol	245	1845(6-29)	0908(6-30)	863	863	-
A-9 (G-36)	N Side of Elder Ferry Rd., ∿ 0.2 km N.E. of Thiokol	55	1900(6-29)	0925(6-30)	865	865	BCEXM
A-10 (G-9)	W side of Elder Ferry Rd., ∿ 33 m E of Thiokol	90	1907(6-29)	0930(6-30)	863	863	BCEXM
A-11 (G-16)	Spiked with 100 µl of BCE Standard	-	-	-	-	-	Section 7.2.1
A-12 (G-19)	Control	-	-	-	-	-	Section 7.2.1

shower (∿5 min) occurred during the sampling. Wind speed and direction data supplied by the weather bureau at Mobile, Alabama Airport are shown in Table 43. The wind was primarily from the south to south-southwest at 5 to 30 km/hr.

Air samples were capped, wrapped to protect against breakage, and returned by air freight to Dayton. Air samples A-1 through A-5, A-7, A-8 and A-10 were solvent desorbed with methanol. Four cm^3 of methanol was used to desorb each tube. The methanol solutions were then analyzed by GC/MS/SIM. Air samples A-7 and A-10 were found to contain bis(2-chloroethoxy) methane. These two samples were located close to the plant (∿ 33 m from the plant) and downwind from the plant. The concentrations of BCEXM found in these samples were 3.1×10^{-6} g/m^3 for A-7 and 8.4×10^{-6} g/m^3 for A-10. No responses were recorded for the six β-chloroethers in the other samples analyzed by solvent desorption (average detection limit = 7×10^{-7} g/m^3 for day samples and 3.8×10^{-7} g/m^3 for night samples). Air sample A-6 was lost during transit. Air sample A-9 was thermally desorbed and characterized by GC/MS. A trace of BCEXM was detected in this sample when the m/e 93 and 63 ions for BCEXM were recalled for this sample. (Average detection limit for this sample was 2×10^{-7} g/m^3). The total ion chromatogram for this sample is shown in Figure 63. The identity of the peaks in the chromatogram are also included in the same figure. Compounds found to be present in this sample were:

- methylene chloride
- benzene
- toluene
- xylene
- methyl ethyl benzene

TABLE 43. WEATHER CONDITIONS DURING SAMPLING AT THIOKOL CORPORATION, MOSS POINT, MISS. 21-35°C

Time (Date)	Wind Speed, km/hr	Wind Direction, degrees
June 29, 1977		
0854	20.4	230
0941	14.8	250
1055	9.3	310
1155	13.0	210
1257	16.7	200
1336	22.2	220
1355	24.1	190
1453	29.6	190
1557	27.8	180
1657	27.8	200
1757	14.8	200
1854	11.1	190
1954	7.4	190
2058	25.9	080
2156	5.6	060
2254	16.7	190
2355	14.8	200
June 30, 1977		
0057	9.3	200
0152	11.1	200
0255	7.4	180
0352	7.4	200
0453	7.4	180
0556	11.1	220
0656	16.7	240
0754	14.8	230
0855	14.8	250
0954	9.3	180

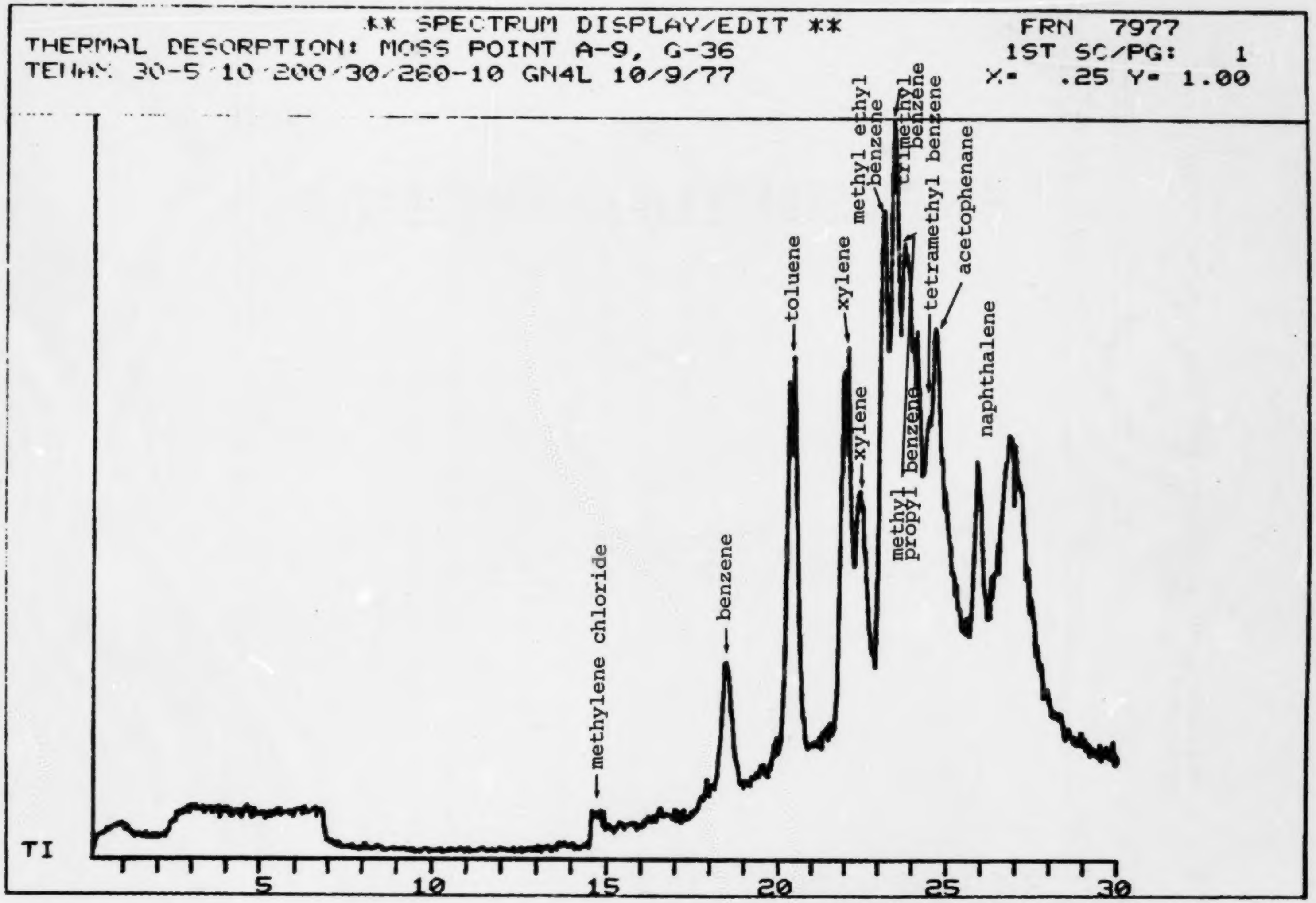


Figure 63. Total ion reconstructed chromatogram of air sample A-9, Thiokol Corporation, Moss Point, Mississippi.

- trimethyl benzene
- methyl propyl benzene
- tetramethyl benzene
- acetophenone
- napthalene

Results for the spike samples are described in Section 7.2.1.

12.2.2 Water Samples

A total of seven water samples were collected in the area of Thiokol Corporation, Moss Point, Mississippi. Two 24-hour composite (one upstream and one downstream) were collected. Three 4-liter grab samples (one downstream and two at the outfall) were also collected. Two 1-liter grab samples were taken at the upstream location (one sample was spiked with a mixture of the β-chloroether and one served as a control). A complete description of the sample location, times, volumes and β-chloroethers found are listed in Table 43. The sample locations are also shown on the topographical map of the area on Figure 64. The river was ∿ 75 m wide at the downstream #1 site, ∿ 100 m at downstream #2, ∿ 75 m at the upstream site, and the outfall was ∿ 2 m wide. Photographs of the drainage ditch, outfall ditch and downstream #1 site are shown in Figure 65. The samples were sealed, placed in an ice chest with foam and ice and the chest was sealed and shipped to MRC-Dayton.

One liter of each sample was extracted three times with 100 cm^3 portions of methylene chloride. These three extracts were combined, concentrated to a volume of ∿ 2.5 cm^3 in a Kuderna-Danish evaporator and analyzed by GC/MS/SIM. The β-chloroethers found in the samples and their concentrations are listed in Table 44. Figure 66 is the SIM chromatogram showing the off-

TABLE 44. WATER SAMPLING AT THIOKOL CORPORATION, MOSS POINT, MISSISSIPPI ON 29-30 JUNE 1977

Sample	Location	Sampling			Volume, *l*	β-chloroethers detected
		Start time	End time	Duration, min		
W-1	Downstream #1 from Thiokol outfall, N side of Escatawpa River, 0.1 km downstream from outfall	0810 (6-29)	0920 (6-30)	1510	4	BCEXM
W-2	Upstream from Thiokol, S side of Escatawpa River, 0.1 km W of International Paper Co.	0090 (6-29)	0940 (6-30)	1420	4	none
W-3	Thiokol outfall at Elder Ferry Rd.	1030 (6-29) Grab	-	-	4	BCEXM BCEE
W-4	Downstream #2 at MS 63 bridge, S side of Escatawpa River	1200 (6-29) Grab	-	-	4	BCEXM
W-5	Same as W-2 spiked	940 (6-30) Grab	-	-	1	See Section 7.2.2
W-6	Same as W-2 control	940 (6-30) Grab	-	-	1	BCEXM
W-7	Thiokol outfall at Elder Ferry Rd.	1000 (6-30) Grab	-	-	4	BCEXM

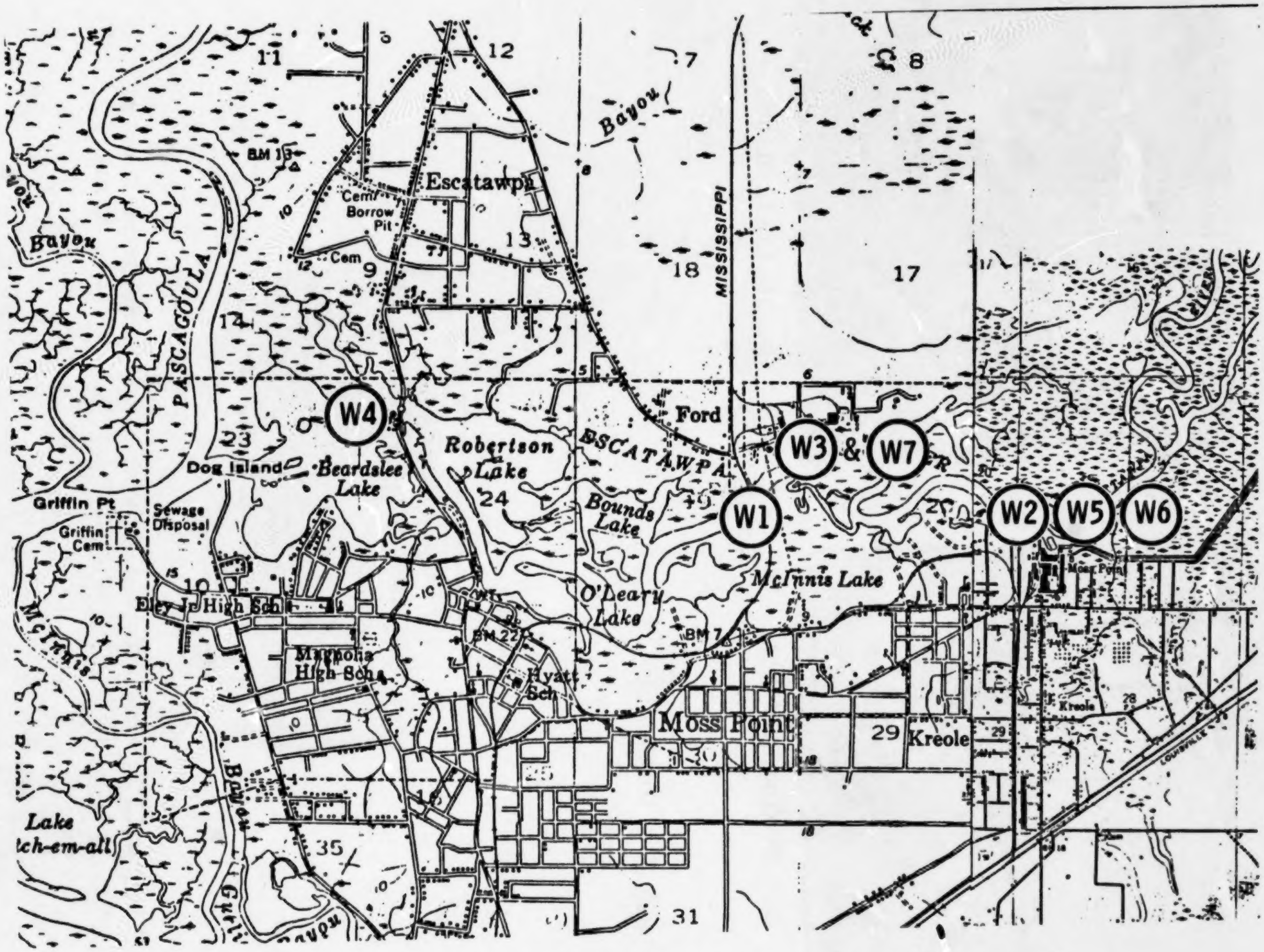
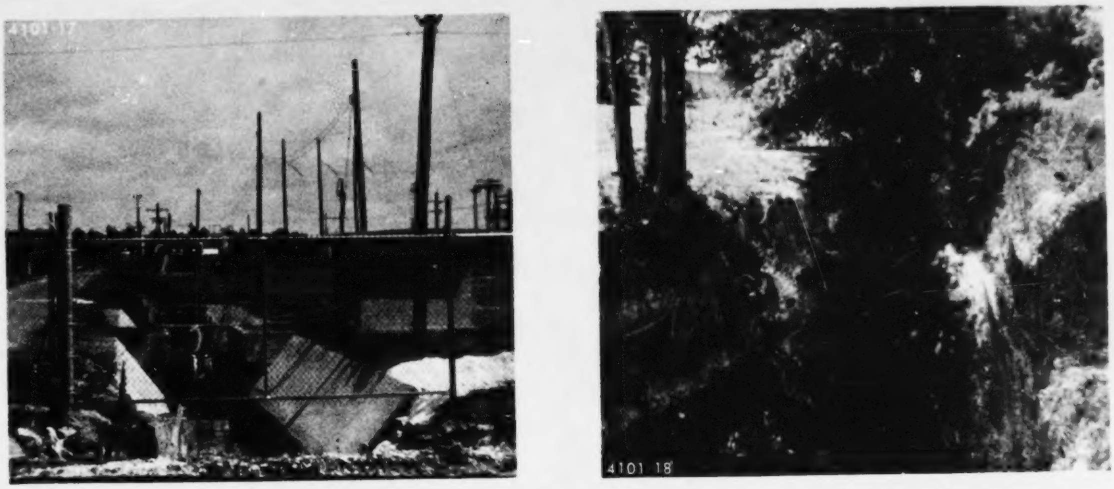
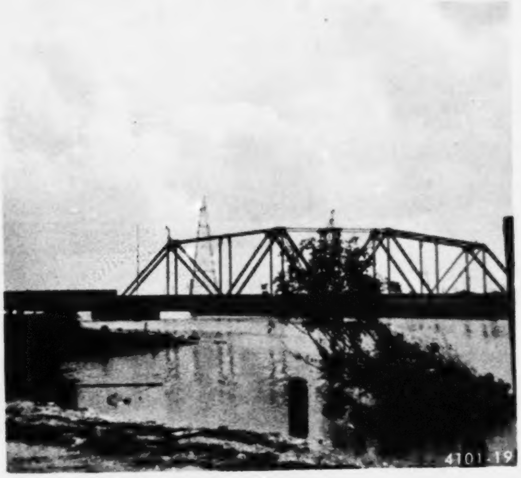

W1
W2
W3 & W7
W4
W5
W6
Escatawpa
Cem
Borrow Pit
BM 13
Bayou
PASCAGOULA
Dog Island
Beardslee Lake
Griffin Pt
Sewage Disposal
Griffin Cem
Eley Jr High Sch
Magnolia High Sch
Robertson Lake
ESCATAWPA R
Ford
Bounds Lake
O'Leary Lake
McInnis Lake
MISSISSIPPI
BM 7
BM 22
Hyatt Sch
Moss Point
Kreole
Lake
Bayou
11
12
7
8
13
18
17
9
23
24
10
29
25
35
31

Figure 64. Location of water samplers at Thiokol Corporation, Moss Point, Mississippi.


4101-17
4101 18

a. Drainage ditch

b. Outfall ditch



c. Downstream #1

Figure 65. Photographs of water sampling locations at Thiakol Corporation, Moss Point, Miss.

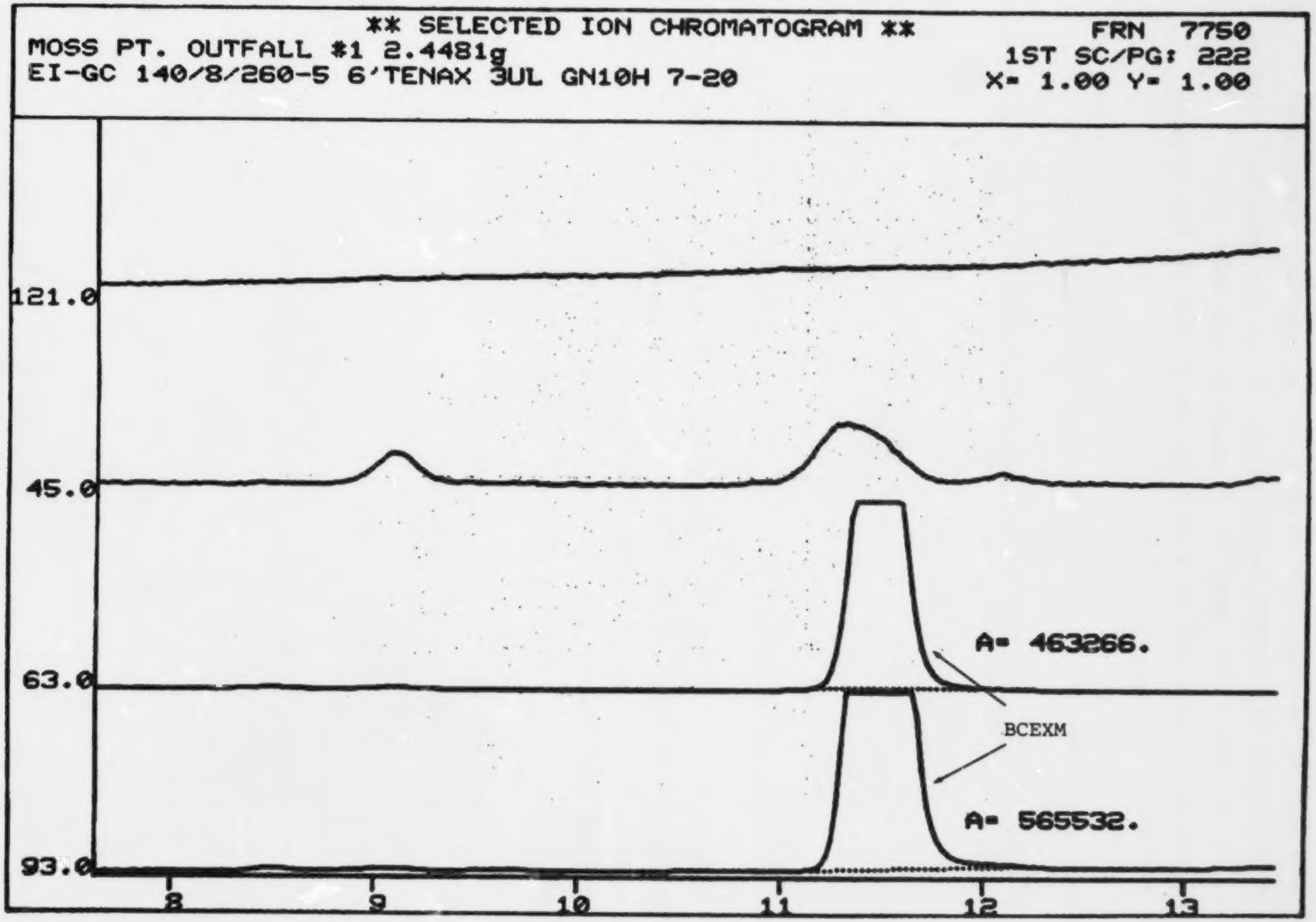


Figure 66. SIM chromatogram of Thiokol Corporation outfall sample #1 (W-3), Moss Point, Mississippi showing BCEXM ions.

scale peaks for BCEXM ions m/e 93 and 63 for outfall sample #1 (W-3). The reason for BCEXM being detected in the control sample upstream can be explained when it is remembered that the Escatawpa River is subject to tidal currents due to the proximity to the Gulf of Mexico.

Table 45. β-CHLOROETHERS FOUND IN MOSS POINT WATER SAMPLES

Sample	Description	BCEE	BCEXM
W-1	Downstream #1		2.5×10^{-7} g/l
W-2	Upstream #1		-
W-3	Outfall #1	6×10^{-7} g/l	1.4×10^{-4} g/l
W-4	Downstream #2		5×10^{-7} g/l
W-6	Control-upstream		7.5×10^{-7} g/l
W-7	Outfall #2		1.5×10^{-4} g/l

Outfall sample #1 (W-3) was also analyzed by GC/MS with the MS operating in the scanned mode. The total ion reconstructed chromatogram for this sample when chromatographed on a 1% SP 2250 column is shown in Figure 67. Peaks in the chromatogram were identified as shown in the figure. Compounds found were:

- 1,4 oxathione
- bis(2-chloroethoxy) methane
- unknown (RT=10 min)
- methyl-di-tert-butyl phenol
- unknown (RT=14.5 min)
- hydrocarbon (probably C_{10} alkane RT=19.7 min)
- hydrocarbon (RT=21.2 min)
- hydrocarbon (RT=22.4 min)
- unknown (RT=22.6 min)
- triphenyl phosphine oxide
- unknown (RT=26 min)

The mass spectra for BCEXM and the unknown at a retention time of 10.0 minutes are shown in Figure 68. Results for the spiked samples are reported in Section 7.2.2.

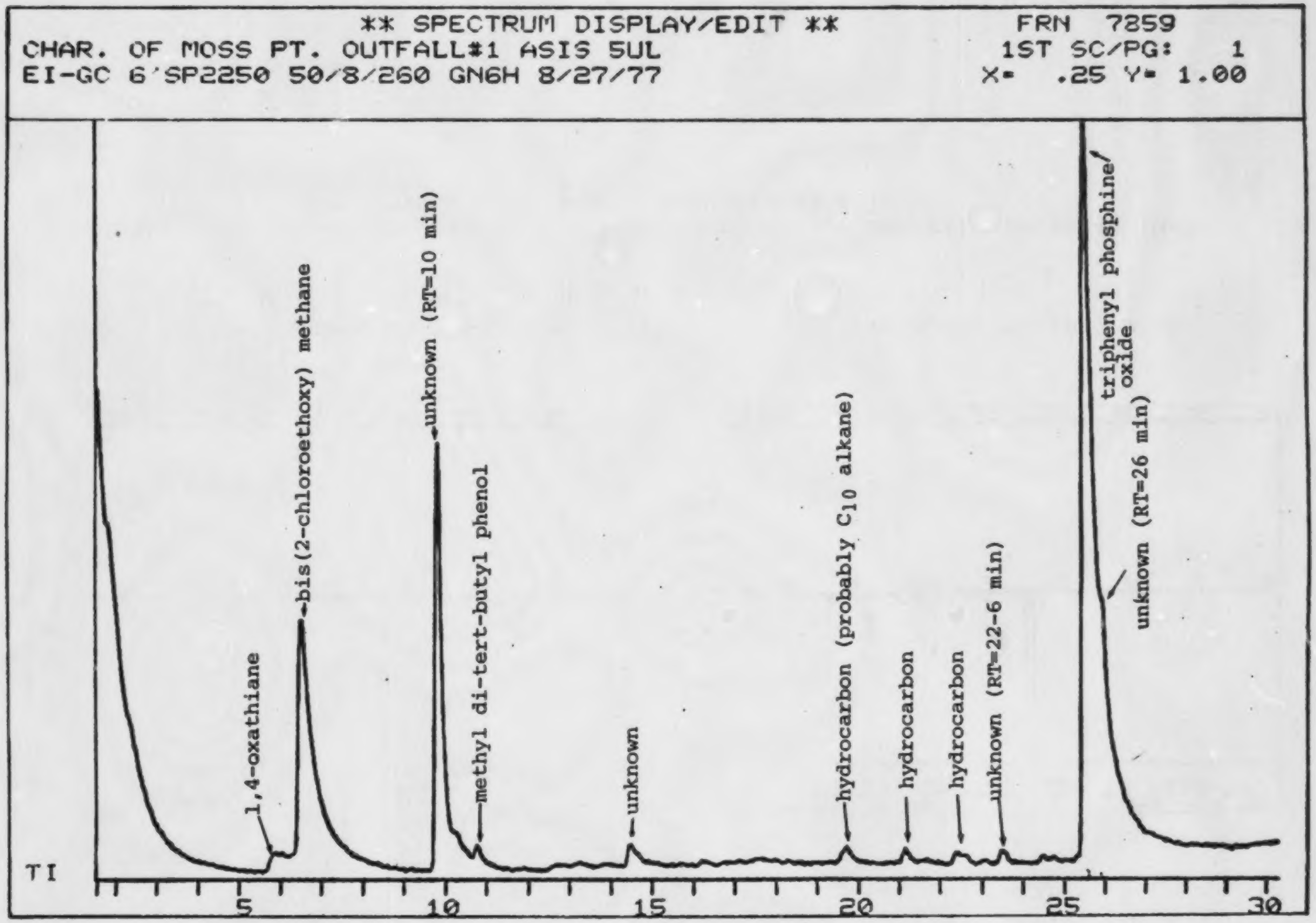
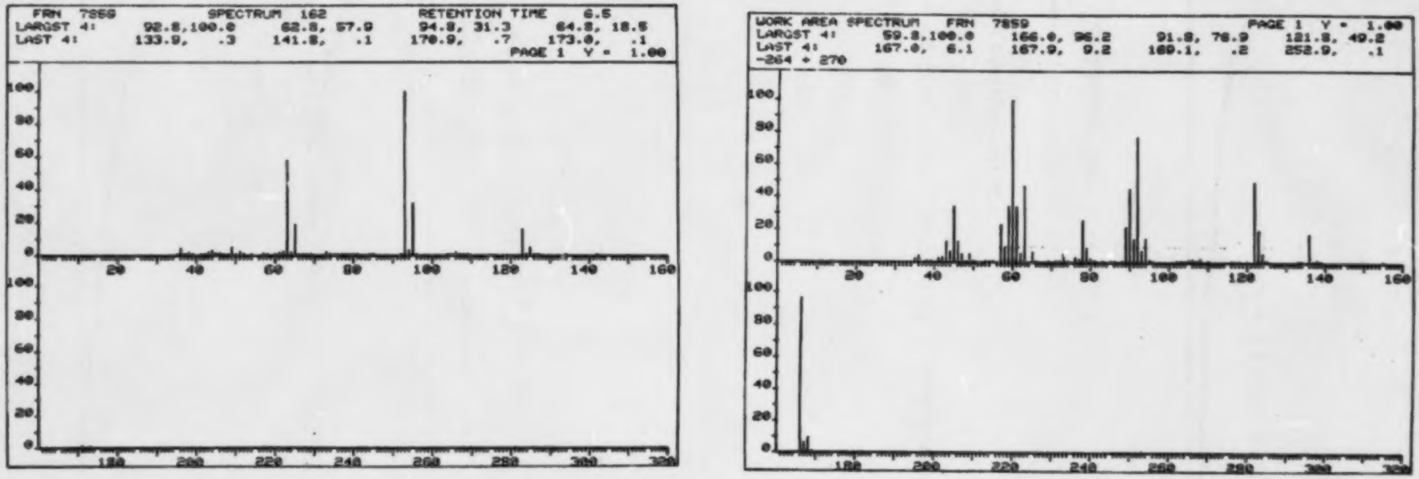


Figure 67. Total ion reconstructed chromatogram of Thiokol Corporation outfall sample #1, Moss Point, Mississippi.



(a) bis(2-chloroethoxy) methane

(b) unknown (RT=10.0 min)

Figure 68. Mass spectra from Thiokol Corporation outfall sample #1 (W-3), Moss Point, Mississippi (see Figure 67).

12.2.3 Soil and Sediment Samples

Soil samples were taken at the locations shown on Figure 69. in the area around Thiokol Corporation, Moss Point, Mississippi. Also sediment samples were taken at the locations shown on Figure 70. The samples were worked up as described in Section 5. Soil samples S-3, S-4, S-5, S-6, S-8 and S-9 and the three sediment samples were analyzed by GC/MS/SIM. Soil sample, S-6, the sample closest to the plant was found to contain 5.8×10^{-7}g/g of BCEXM. Two of the sediment samples, SD-1 the outfall sample and SD-2 the upstream location, were both found to contain BCEE and BCEXM. The concentrations were SD-1, BCEE=6.8×10^{-8} g/g and BCEXM=1.4×10^{-7} g/g and and SD-2, BCEE=1.0×10^{-8} g/g and BCEXM=2.3×10^{-7} g/g.

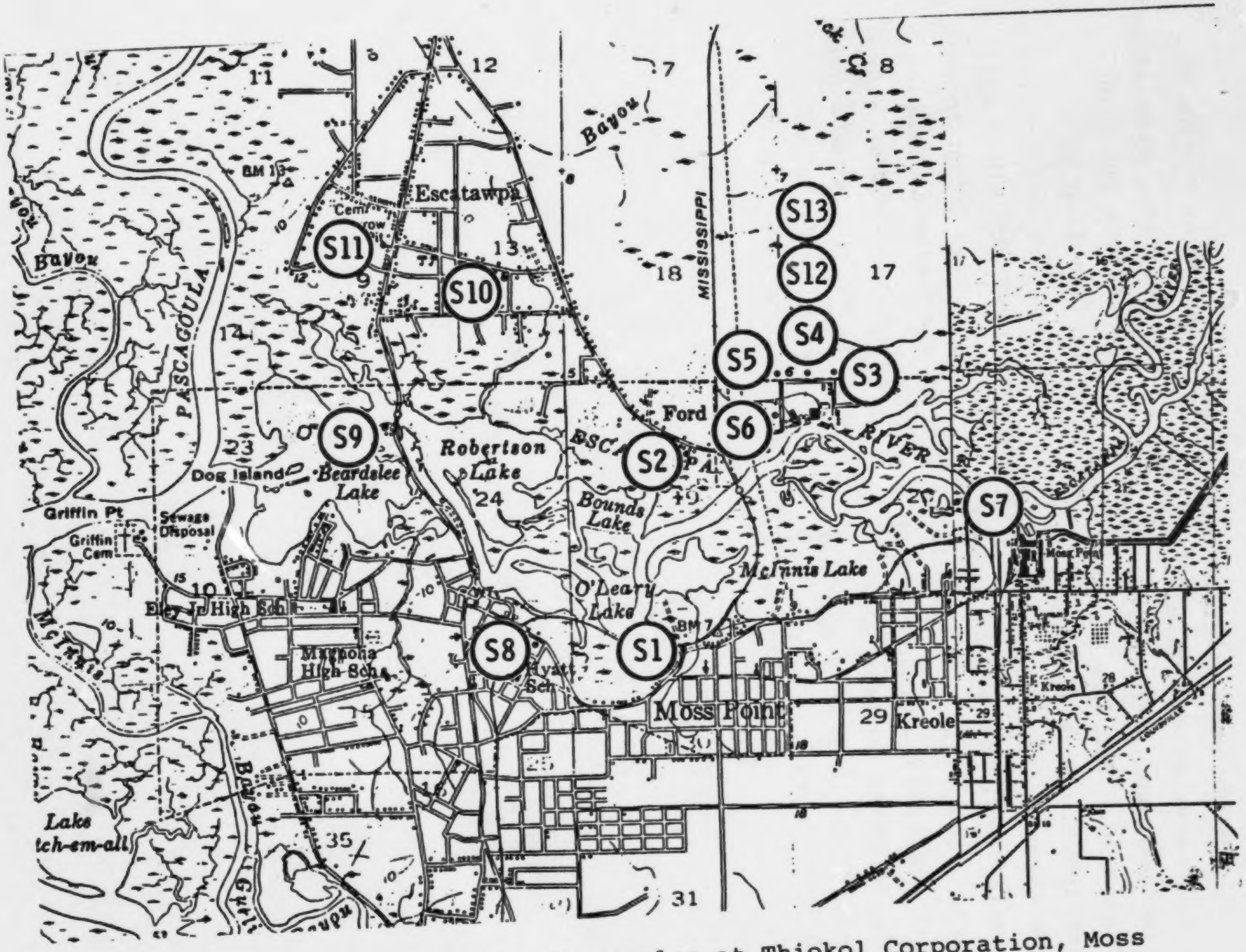

S1
S2
S3
S4
S5
S6
S7
S8
S9
S10
S11
S12
S13
Escatawpa
Bayou
MISSISSIPPI
PASCAGOULA
ESCATAWPA RIVER
Ford
Robertson Lake
Bounds Lake
O'Leary Lake
McInnis Lake
Beardslee Lake
Dog Island
Griffin Pt
Griffin Cem
Sewage Disposal
Moss Point
Kreole
Magnolia High Sch
Hyatt Sch
Eley Jr High Sch
Lake
Bayou
7
8
11
12
13
14
17
18
23
24
29
31
35

Figure 69. Location of soil samples at Thiokol Corporation, Moss Point, Mississippi.

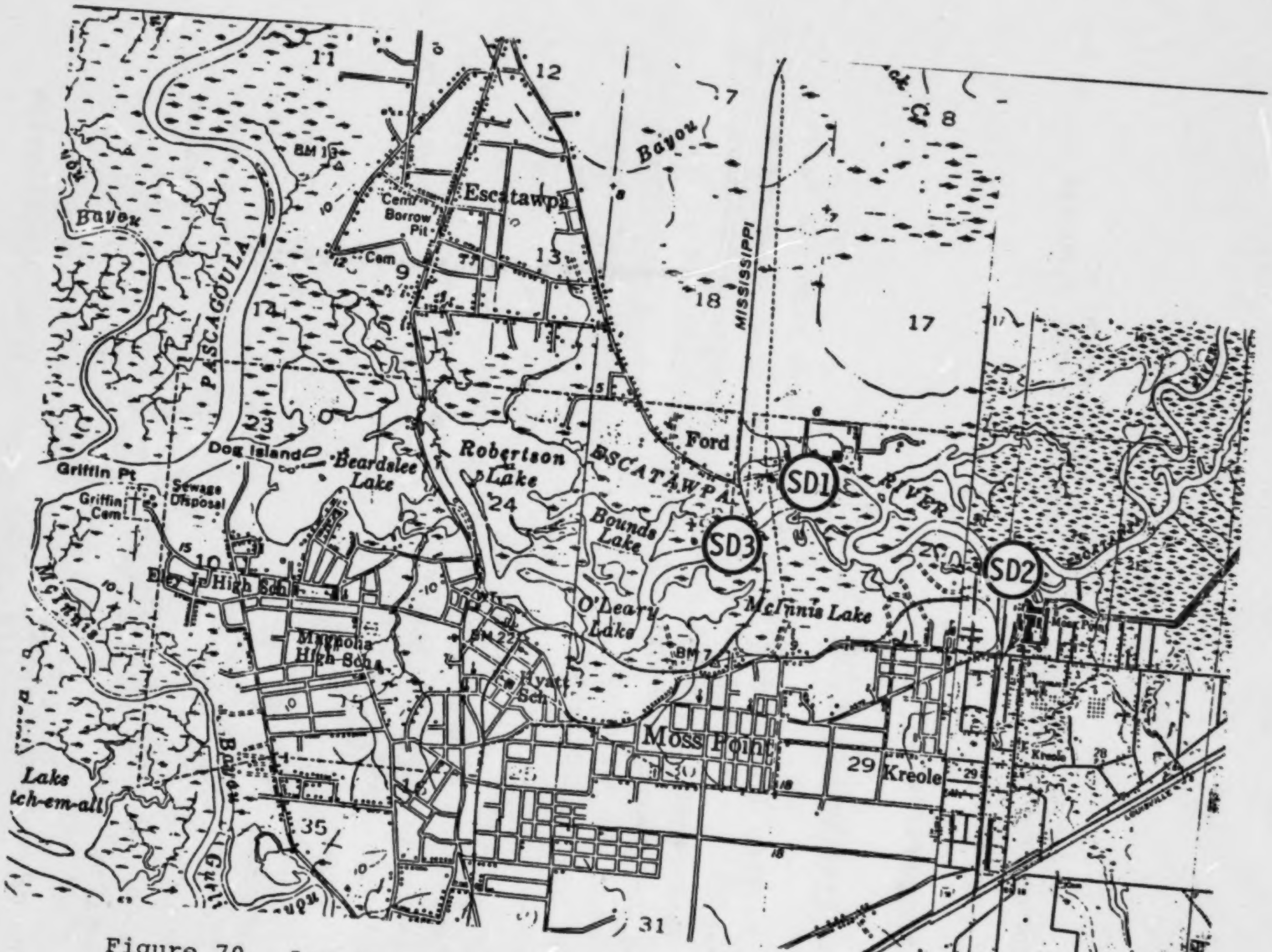

SD1
SD2
SD3
ESCATAWPA RIVER
PASCAGOULA
MISSISSIPPI
Escatawpa
Moss Point
Kreole
Robertson Lake
Beardslee Lake
Bounds Lake
O'Leary Lake
McInnis Lake
Dog Island
Griffin Pt
Griffin Cem
Sewage Disposal
Cem Borrow Pit
Bayou
Ford
Magnolia High Sch
Hyatt Sch
Lakes
Bayou
BM 7
BM 22
7
8
9
11
12
13
17
18
23
24
29
30
31
35

Figure 70. Location of sediment samples at Thiokol Corporation, Moss Point, Mississippi.

SECTION 13

SAMPLING AND ANALYSIS FOR β-CHLOROETHERS AT UNION CARBIDE CORPORATION, INSTITUTE, WEST VIRGINIA

13.1 PRESAMPLING SURVEY

13.1.1 Description of the Plant Site

Union Carbide Corporation is located on West Virginia Route 25 West of Institute, West Virginia. The plant produces a wide variety of industrial organic and inorganic chemicals. Among the compounds reported to have been produced at the site over the years are ethylene chlorohydrin, ethylene oxide, bis(2-chloroethyl) ether, 2-chloroethyl vinyl ether, propylene oxide, bis(2-chloroisopropyl) ether, and 1,2-bis(2-chloroethoxy) ethane (1, 45). While most recent reports tended to indicate ethylene oxide and propylene oxide are no longer produced at this site or the Union Carbide South Charleston plant, the production status of the β-chloroethers was unknown.

A presurvey of the plant area was performed on August 18, 1977. The presurvey consisted of visual inspection of the Union Carbide complex, since contact with plant personnel was not allowed, and selection of sites for air and water sampling.

The Union Carbide complex at Institute is a series of buildings of open and closed construction, distillation towers, cooling towers, liquid storage tanks and a power plant. The location of the complex is illustrated on the topographical map of the area in Figure 71. Union Carbide occupies the area between West Virginia 25 and the Kanawha River at the west edge of Institute, West Virginia. The plant property encompasses an area ∿2.4 km long (NW to SE) and ∿0.5 km wide (NE to SW). Figure 72 shows the dimensions of the area on the topographical map. The complex is bounded on the north by WV 25, on the east by the West Virginia Rehabilitation Center, on the south by the Kanawha River and on the west by a scrap iron company and open fields. Figure 73 is a panoramic photograph of the Union Carbide complex. The photograph was taken from a hill north of the complex.

13.1.2 Surrounding Area

The Institute area is located on the north bank of the Kanawha River in west central West Virginia approximately 10 km west of Charleston, W. Va. Elevation of the area ranges from 175 m at the river to 325m at the tops of surrounding hills. The whole area is a series of hills and valleys enclosing the entire Kanawha River valley. To the east of the plant are the towns by Institute (pop. 2700), Dunbar (pop. 9151) and the city of Charleston (pop. 71,505). Southwest of the plant is Saint Albans (pop. 14,356). To the west is of the complex is Nitro (pop. 8019). Directly north of the Union Carbide site is a series of steep hills with a very few single family dwellings.

Industry in the immediate area of the Union Carbide complex included Appalachian Power's Turner station, Criss and Shaver and Kim Ballard Machine. Other major chemical plants upstream from Carbide are Du Pont, FMC and the Union Carbide South Charleston plant.

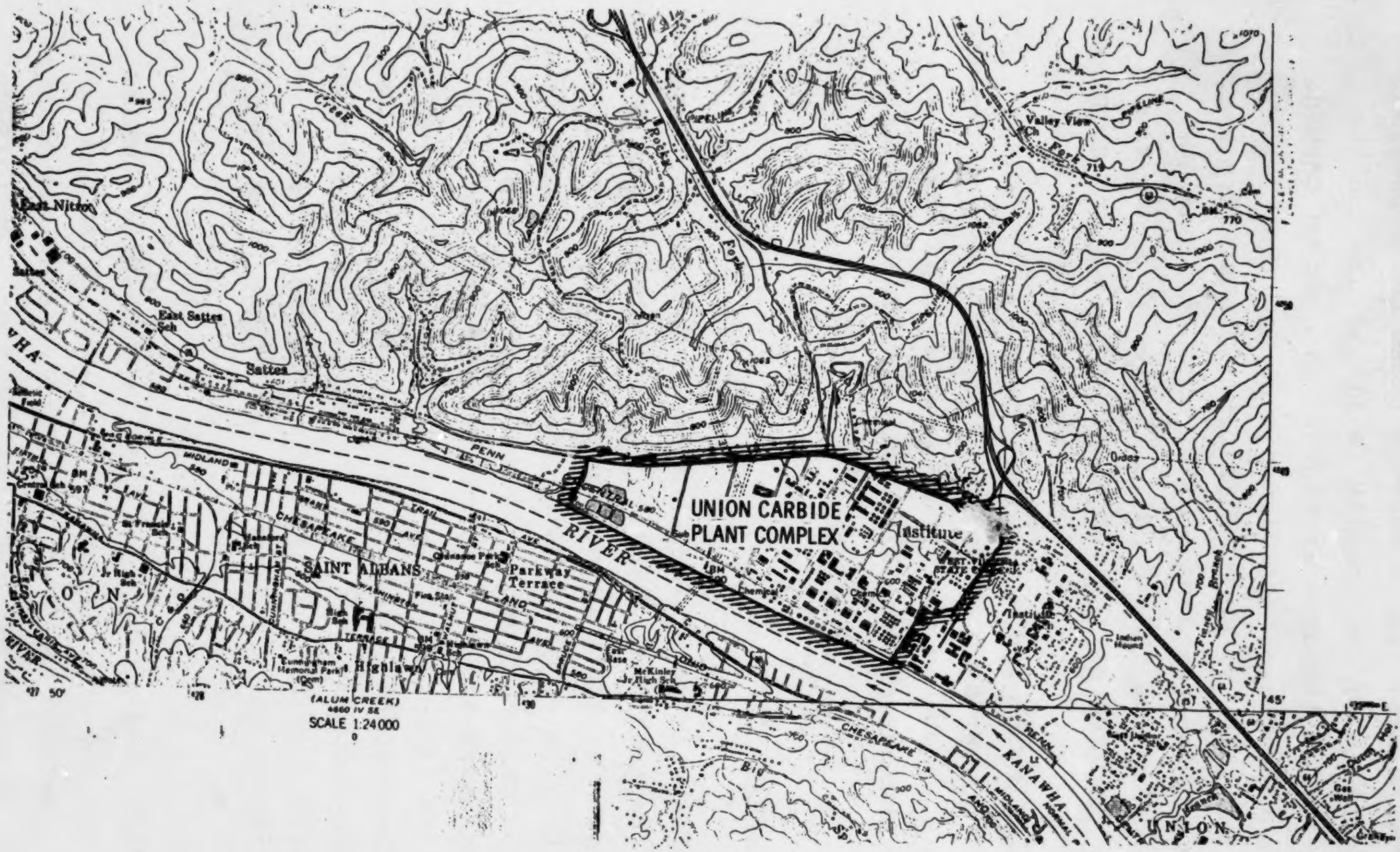

UNION CARBIDE
PLANT COMPLEX
Institute
RIVER
KANAWHA
SAINT ALBANS
Parkway Terrace
Highlawn
East Nitro
Sattes
East Sattes Sch
Valley View Ch
Rocky Fork
Creek
PENN
CHESAPEAKE
MIDLAND
McKinley Jr High Sch
UNION
(ALUM CREEK)
SCALE 1:24000

Figure 71. Location of Union Carbide Corporation plant on topographical map of Institute, W. Va. area.

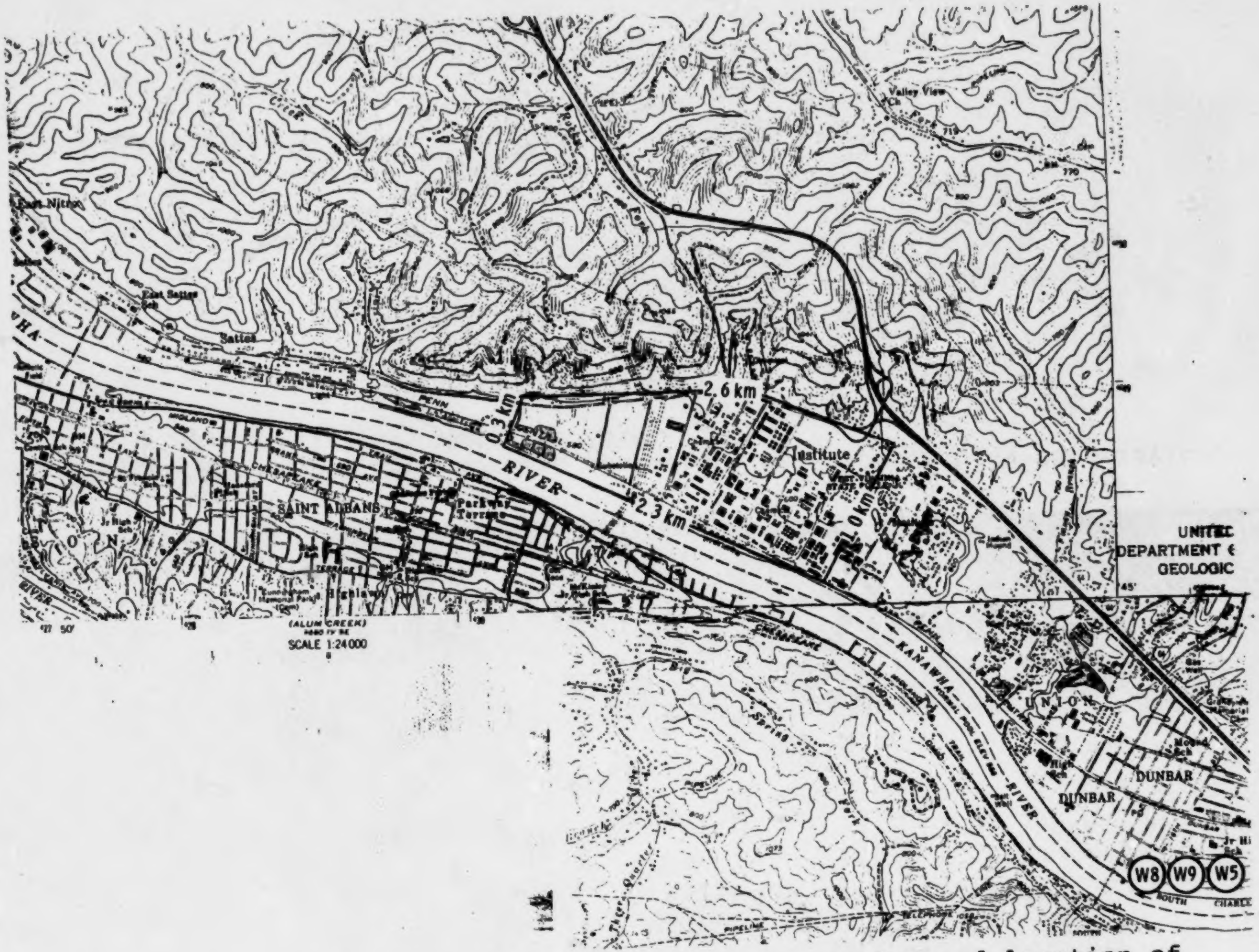

2.6 km
0.3 km
2.3 km
0 km
Institute
RIVER
KANAWHA
RIVER
SAINT ALBANS
Parkway Terrace
East Nitro
Sattes
UNITED
DEPARTMENT
GEOLOGIC
UNION
DUNBAR
DUNBAR
W8
W9
W5
SCALE 1:24000
ALUM CREEK

Figure 72. Dimensions of the Union Carbide complex and location of upstream water samples at Institute, W. Va.

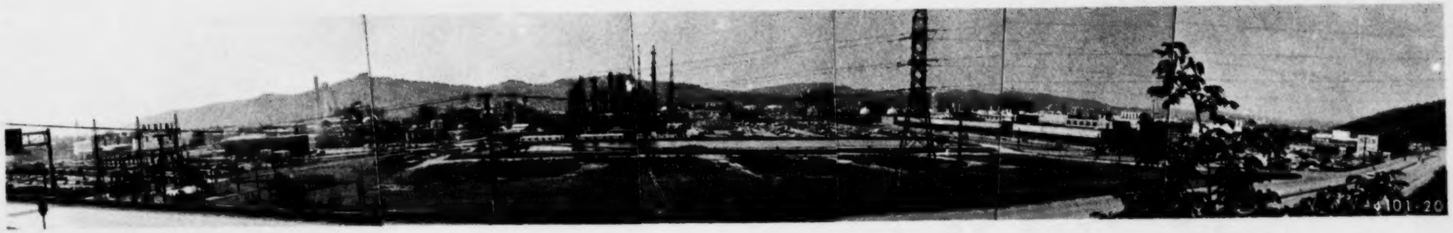


Figure 73. Composite panoramic photograph of Union Carbide Corporation, Institute, West Virginia.

Vegetation in the area includes a number of species of deciduous trees (including oaks and elms), bushes and weedy ground cover. The banks on the south side of the Kanawha River downstream from the Union Carbide plant are extremely steep. In addition the north bank of the river is completely lined with private single family dwellings.

Visible emissions from the plant included steam from various vents and stacks, gray smoke from the power plant and a very dense white smoke tinged yellowish brown from a small plant on the north side of WV 25. This plume had a very strong nitric acid odor. Also a very strong, indistinct odor was coming from the Carbide plant proper.

13.2 SAMPLING AND ANALYSIS RESULT

Sampling of the area around Union Carbide Corporation, Institute, West Virginia for β-chloroethers was conducted on 18-19 August 1977. The conditions, locations and results for air, water, soil and sediment samples collected during this sampling trip are contained in the following subsections.

13.2.1 Air Samples

Air samplers were placed around the Union Carbide plant in the configuration shown in Figure 74. Seven samplers of the personnel sampling type described in Section 4.1, were used for sampling for β-chloroethers in the air around Carbide during the day light on 18 August 1977. β-Chloroethers were collected on the large style Tenax GC tubes; a charcoal tube was used as backup. Three samples were collected using the same type samplers during the night of 18-19 August 1977. Weather was good during daylight hours with winds light and variable and a high temperature of 24°C. At night a fog occurred and wind was almost non-existent. Weather data for

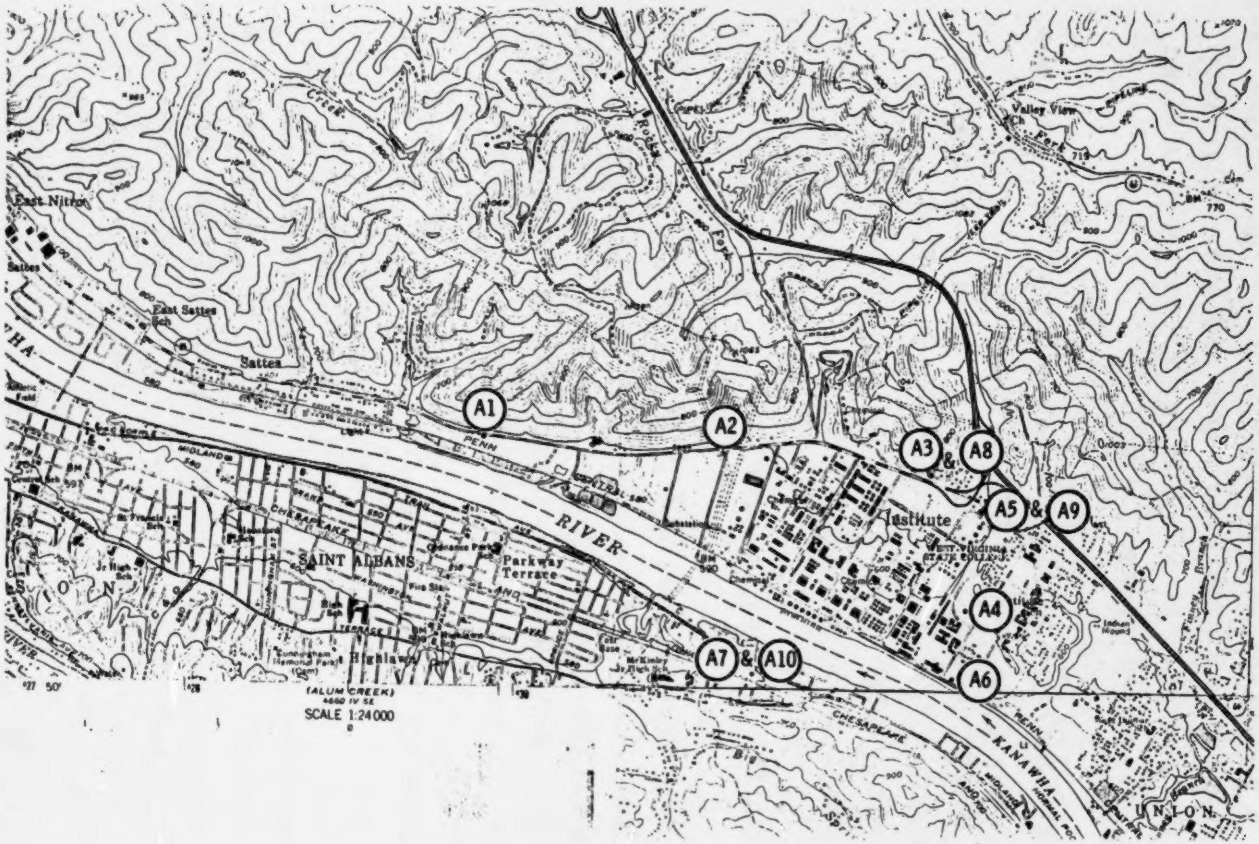

A1
A2
A3
&
A8
A5
&
A9
A4
A6
A7
&
A10
East Nitro
Sattes
East Sattes Sch
PENN
RIVER
KANAWHA
Institute
SAINT ALBANS
Parkway Terrace
Highlawn
Valley View Ch
CHESAPEAKE
UNION
(ALUM CREEK)
4660 IV SE
SCALE 1:24 000

Figure 74. Air sampling locations at Union Carbide, Institute, W. Va.

the sampling periods are shown in Table 46. After sampling the tubes were capped with polyethylene slip-on type caps and wrapped with paper towels to insure against breakage. Table 47 lists the sample numbers, sampling location, compass reading relative to the center of the plant, sampling start and stop time, duration of sampling, volume of air sampled and β-chloroethers detected.

The tubes were returned to the laboratory and desorbed and analyzed as described in Sections 5 and 6. Air samples A-1, A-2, A-4, A-5, A-6, A-8, A-9, and A-10 were solvent desorbed and analyzed by GC/MS/SIM for the six β-chloroethers. Average detection limit for day samples was 7×10^{-7} g/m^3 and 3.9×10^{-7} g/m^3 for night samples. Air sample A-3 was thermally desorbed for characterization by scanned mass spectrometry. Air sample A-7 was lost during thermal analysis. The total ion reconstructed chromatogram for A-3 is shown in Figure 75. The compounds identified by their mass spectra are shown in the same figure and listed below.

- trichloromonofluoromethane
- methylene chloride
- benzene
- toluene
- chlorobenzene
- ethyl benzene
- isopropyl benzene
- methyl ethyl benzene
- benzaldehyde
- nitrotoluene

TABLE 46. WEATHER CONDITIONS DURING SAMPLING AT UNION CARBIDE, INSTITUTE, W. V. 11-24°C

Time (DATE)	Wind Speed, km/hr	Wind Direction, degrees
August 18, 1977		
1055	5.6	350
1155	3.7	050
1255	11.1	360
1355	9.3	300
1455	9.3	200
1555	5.6	300
1655	11.1	310
1755	11.1	330
1855	9.3	350
1955	5.6	350
2055	5.6	100
2155	0	-
2255	0	-
2355	0	-
August 19, 1977		
0055	0	-
0155	0	-
0255	3.7	080
0355	5.6	040
0455	5.6	090
0555	5.6	090
0655	3.7	050
0755	0	-
0855	0	-
0955	0	-
1055	5.6	340

TABLE 47. AIR SAMPLING AT UNION CARBIDE, INSTITUTE, W.V. ON 18-19 AUGUST 1977

Sample (Tenax Tube)	Location	Compess Reading	Sampling				β-Chloroethers detected
			Time		Duration, min	Volume, liter	
			Start	End			
A1 (G-37)	S side of WV 25, 3 km W of I-64	270	1111 (8-18)	1920 (8-18)	489	489	None
A2 (G-49)	S side of WV 25, 1.6 km W of I-64	300	1125 (8-18)	1930 (8-18)	485	485	None
A3 (G-14)	N side of WV 25, 0.4 km W of I-64	20	1135 (8-18)	1940 (8-18)	485	485	None
A4 (G-13)	WV Rehabilitation Center Campus in Institute, WV - 0.75 km SE of Plant Center	130	1150 (8-18)	1957 (8-18)	487	487	None
A5 (G-24)	S side of WV 25 at intersection with Ave. A, 75m E of I-64 0.85km NE of plant	90	1200 (8-18)	2012 (8-18)	492	492	None
A6 (G-10)	E side of Ave in West Virginia State College campus, 10m from Kanawha R., 0.95 km SE of plant center	140	1219 (8-18)	2005 (8-18)	466	466	None
A7 (G-11)	S side of US 60, 0.35 km W of Kanawha Terrace in St. Albans, W.V., 0.87 km SW of plant	210	1245 (8-18)	2035 (8-18)	470	470	None
A8 (G-41)	N side of WV 25, 0.4 km W of I-64	20	1950 (8-18)	1000 (8-19)	850	850	None
A9 (G-31)	S side of WV 25 at intersection with Ave. A, 75m E of I-64 0.85m NE of plant	90	2023 (8-18)	1010 (8-19)	827	827	None
A10 (G-12)	S side of US 60, 0.35 km W of Kanawha Terrace in St. Albans, W.V., 0.87 km SW of plant	210	2040 (8-18)	930 (8-19)	770	770	None

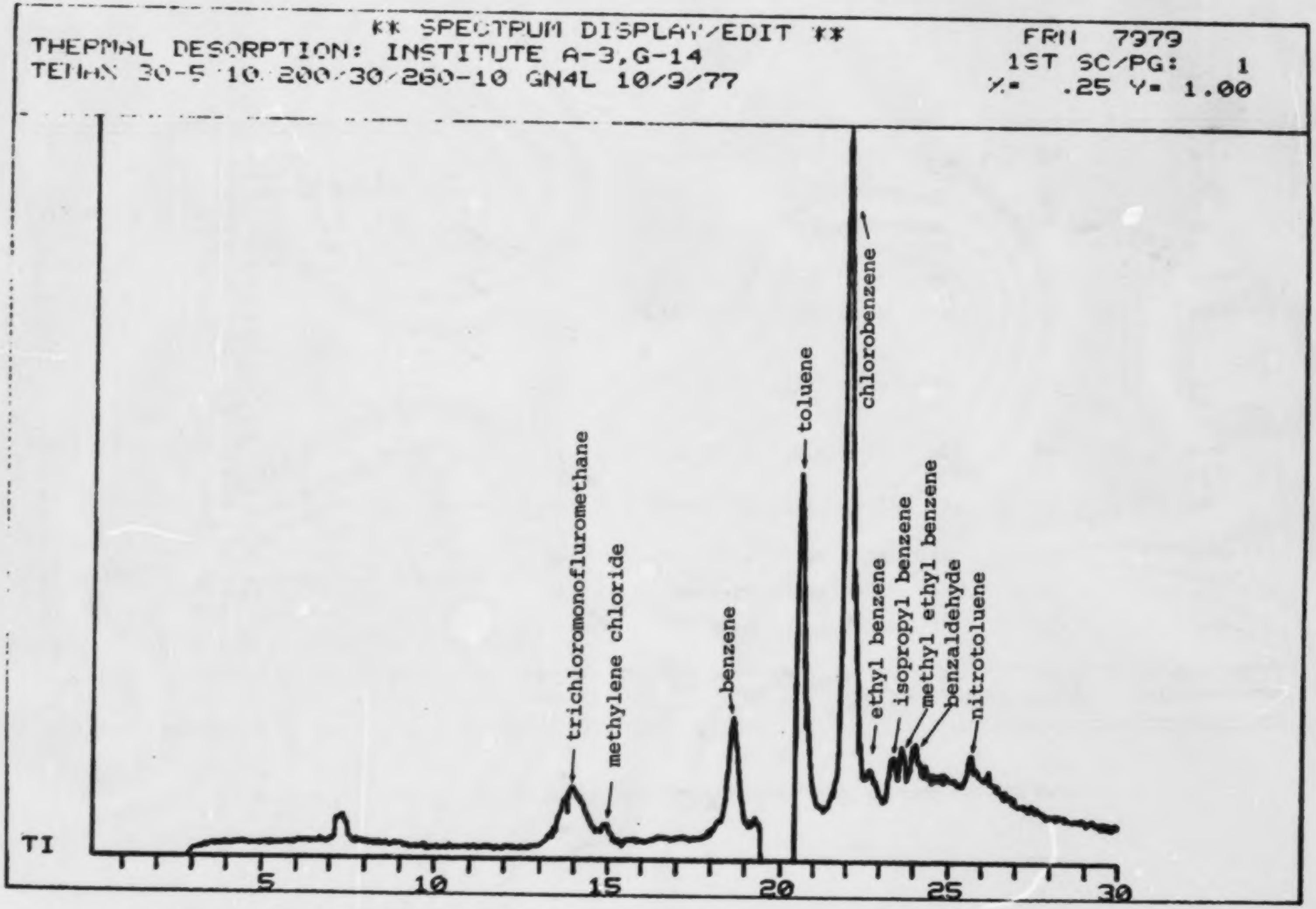
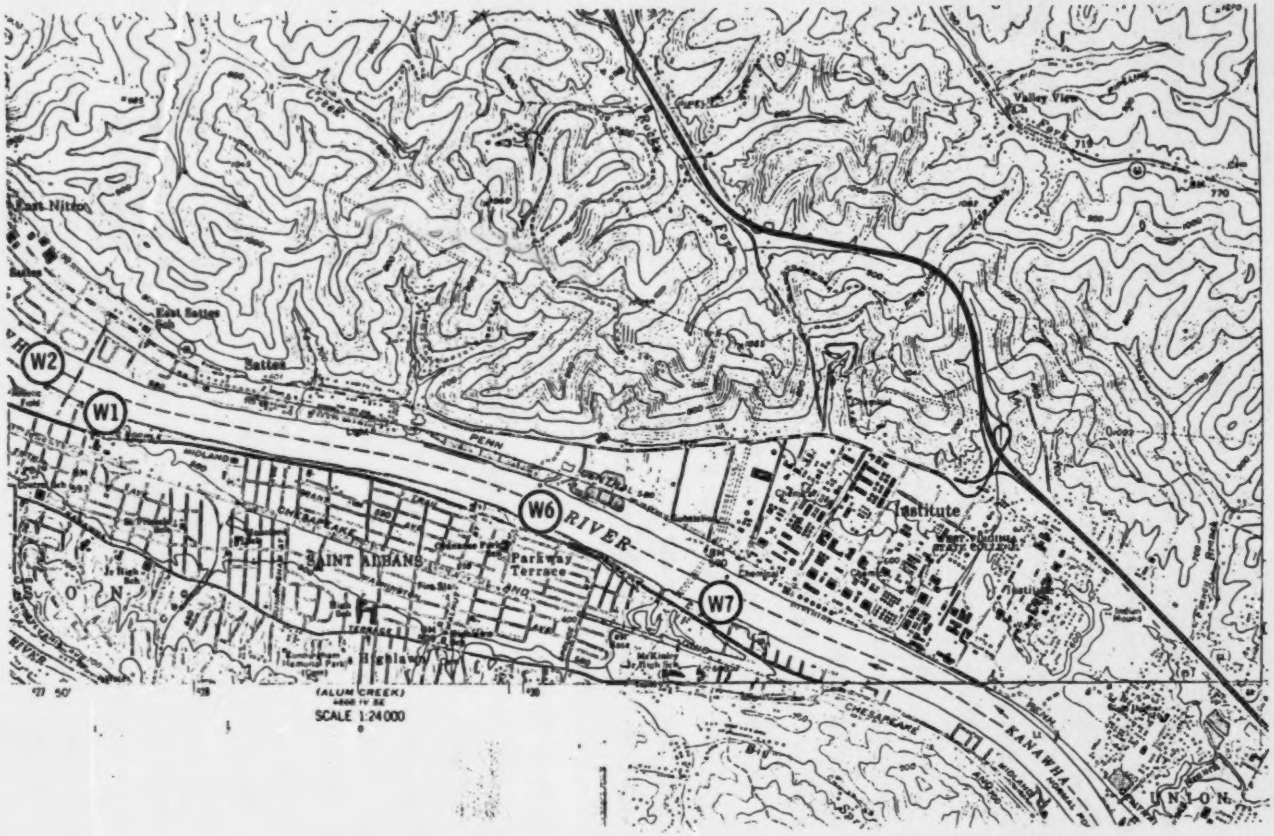


Figure 75. Total ion reconstructed chromatogram of air sample A-3, thermally desorbed, Union Carbide, Institute, W. Va.

13.2.2 Water Samples

Because of the steep south banks of the Kanawha River, which were heavily covered with thorny bushes, and the large population of single family dwellings along the north bank, we were unable to obtain the two downstream and one upstream 24-hour composite water samples desired. One composite 24-hour sample was taken downstream ∿5 km from the Union Carbide outfall. The locations of the other grab water samples taken for the site are shown on the topographical map in Figure 76 for the outfall and downstream samples and Figure 72 for the upstream samples. A description of all of the water sampling sites is included in Table 48. Included in this table are sampling times, volume of sample collected and β-chloroethers detected. Sample W-1, downstream #1, was taken at Mitch's Marina in St. Albans, W.V. on the south bank of the Kanawha. The surface of the river was covered with an oily film. Water sample W-2 was taken as a 24-hr composite sample on the north bank of the Kanawha, behind a Pentacostal church. Water samples W-3, W-4, and W-5 were taken as upstream samples from the north bank of the Kanawha River at 17th Street in Dunbar, W.V., Sample W-4 was spiked β-chloroether standard solution. Water sample W-6 was collected from a boat, 6 m from the north bank of the Kanawha just downstream from the Union Carbide Environmental Center. Sample W-7 was also obtained from the boat 1.5 m downstream from the farthest downstream visible Union Carbide outfall. The Kanawha River was muddy and contained numerous branches, logs and other debris. Local residents stated that areas in the Kanawha watershed had had heavy rains recently. Photographs of the outfalls and the sampling location just downstream from the Union Carbide Environmental Center are shown in Figure 77.

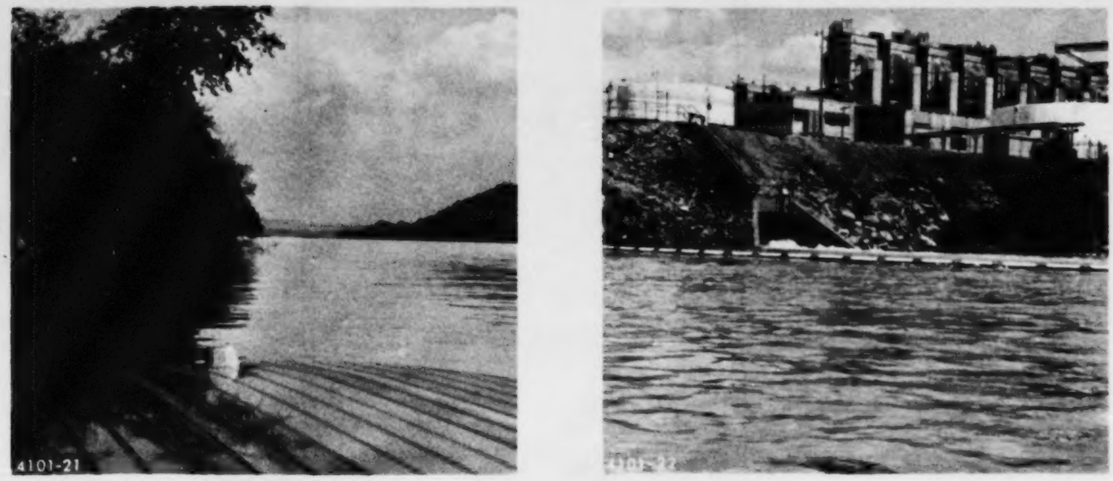


W1
W2
W6
W7
RIVER
KANAWHA
East Nitro
Sattes
Institute
SAINT ALBANS
Parkway Terrace
Valley View
PENN
CHESAPEAKE
UNION
(ALUM CREEK)
SCALE 1:24 000

Figure 76. Downstream and outfall water sampling locations at Union Carbide, Institute, W. Va.

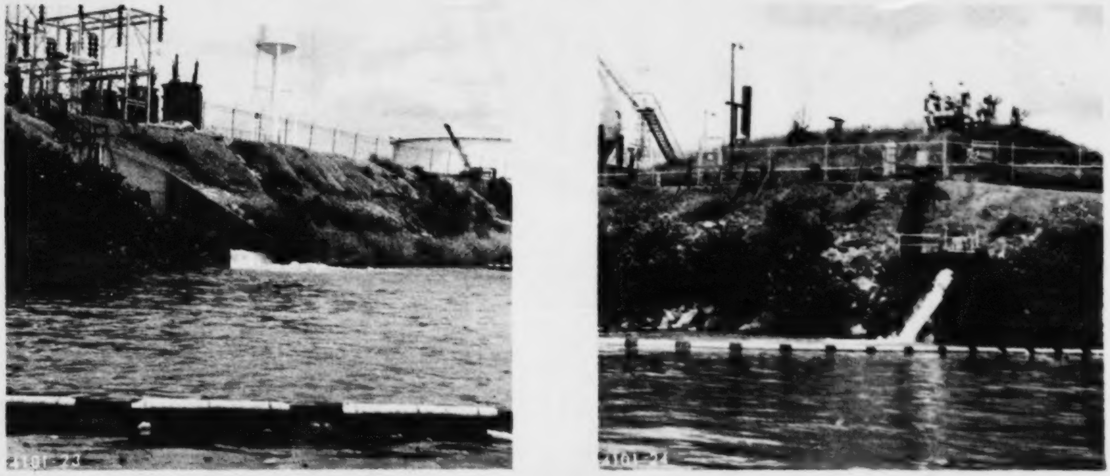
TABLE 48. WATER SAMPLING AT UNION CARBIDE, INSTITUTE, W. V. on 18-19 AUGUST, 1977

Sample	Location	Sample Time Start	Sample Time End	Sample Duration, min	Sample Volume, liter	β-chloroethers detected
W-1	0.1 km E of 3rd St. bridge at Marina	1315 (8-18)	GRAB	-	4	None
W-2	0.3 km W of 3rd St. bridge behind Nazarene Church	1010 (8-18)	945 (8-18)	1415	4	None
W-3	17th St. N bank of Kanawha River - Dunbar, WV	1030 (8-19)	GRAB	-	4	None
W-4	17th St. N bank of Kanawha River - Spike	1030 (8-19)	GRAB	-	1	See Section 7.2.2
W-5	17th St. N bank of Kanawha River - Control	1030 (8-19)	GRAB	-	1	See Section 7.2.2
W-6	Outfall #2 just downstream from Union Carbide Environmental plant	1330 (8-18)	GRAB	-	4	None
W-7	Outfall #1 1.5 m downstream from farthest downstream Union Carbide outfall	1325 (8-18)	GRAB	-	4	None



a. River downstream from Union Carbide Center

b. Outfall downstream #2

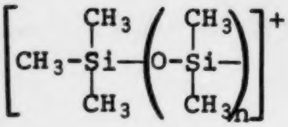


c. Outfall downstream #3

d. Outfall downstream #1

Figure 77. Photographs of water sampling locations and outfall at Union Carbide, Institute, West Virginia.

The samples were extracted, concentrated and analyzed as described in Sections 5 and 6. None of the samples except the spiked upstream sample, W-4 were found to contain β-chloroethers. Results for sample W-4 are reported in Section 7.2.2. The extract of water sample W-7, the sample taken 1.5 m from the farthest downstream of the visible outfalls, was characterized by GC/MS in the scanned mode. The total ion reconstructed chromatogram for this sample is shown in Figure 78. Compounds identified are listed on the figure and below. A series of silicones characterized by m/e ions of 73 and 147 are indicated on Figure 78 by S's. These mass-to-charge ions are characteristic of a series of silicones having the structure shown below (66).



$$\left[CH_3-\overset{CH_3}{\underset{CH_3}{Si}}-\left(O-\overset{CH_3}{\underset{CH_3}{Si}}-\right)_n\right]^+$$

n=0,1,2,3----

m/e	n
73	0
147	1
221	2
295	3

Figure 79 shows the total ion chromatogram and single ion traces for masses 73 and 147 of the silicones.

- dichlorobenzene
- phenyl ether
- 2,2,4-trimethyl penta-1,3-diol diisobutyrate
- diethyl phthalate
- unknown (RT=13.9 min)
- di-n-butyl phthalate
- dioctyl phthalate
- unknown (RT=25 min)

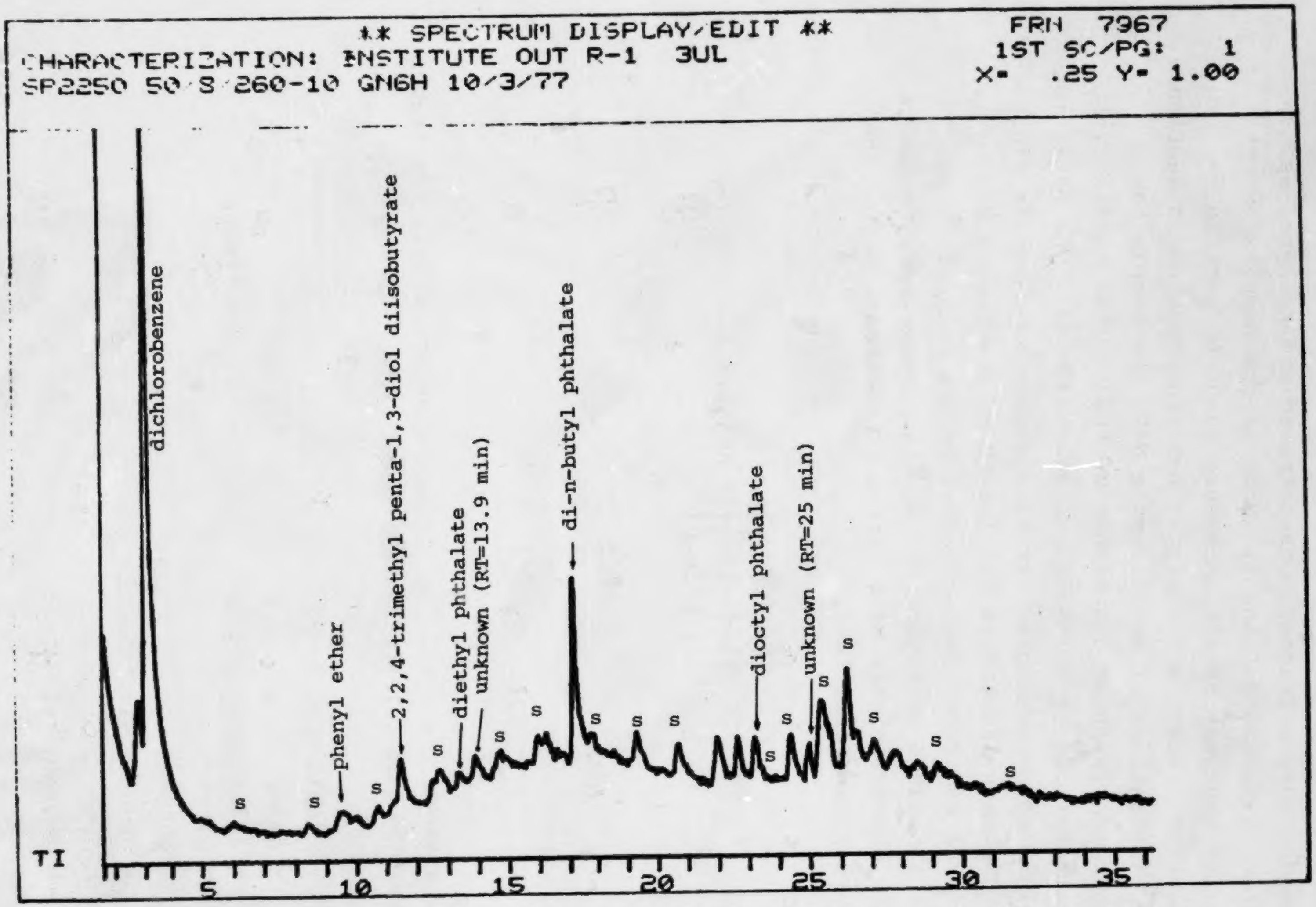


Figure 78. Total ion reconstructed chromatogram of water sample W-7, Union Carbide, Institute, West Virginia.

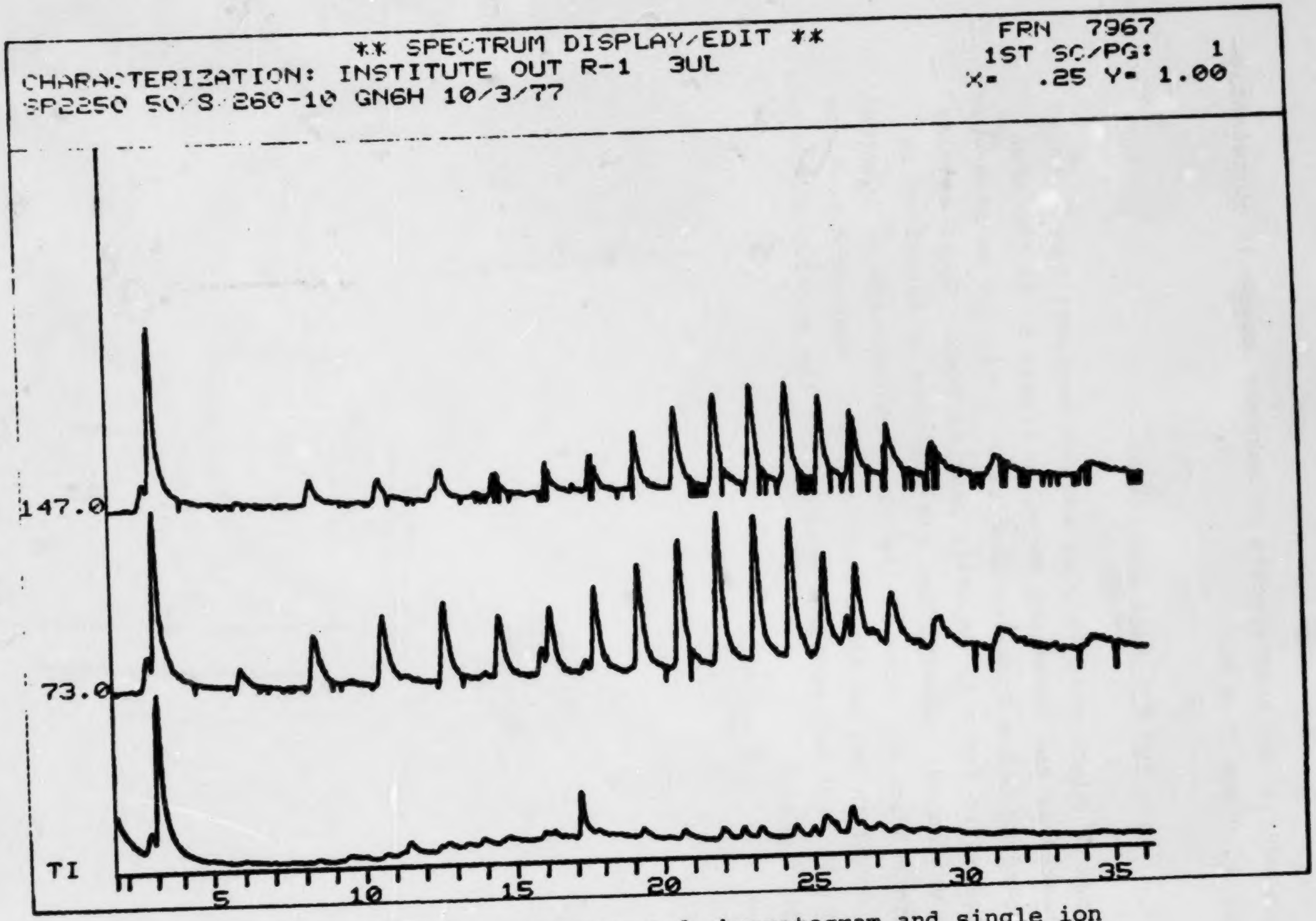
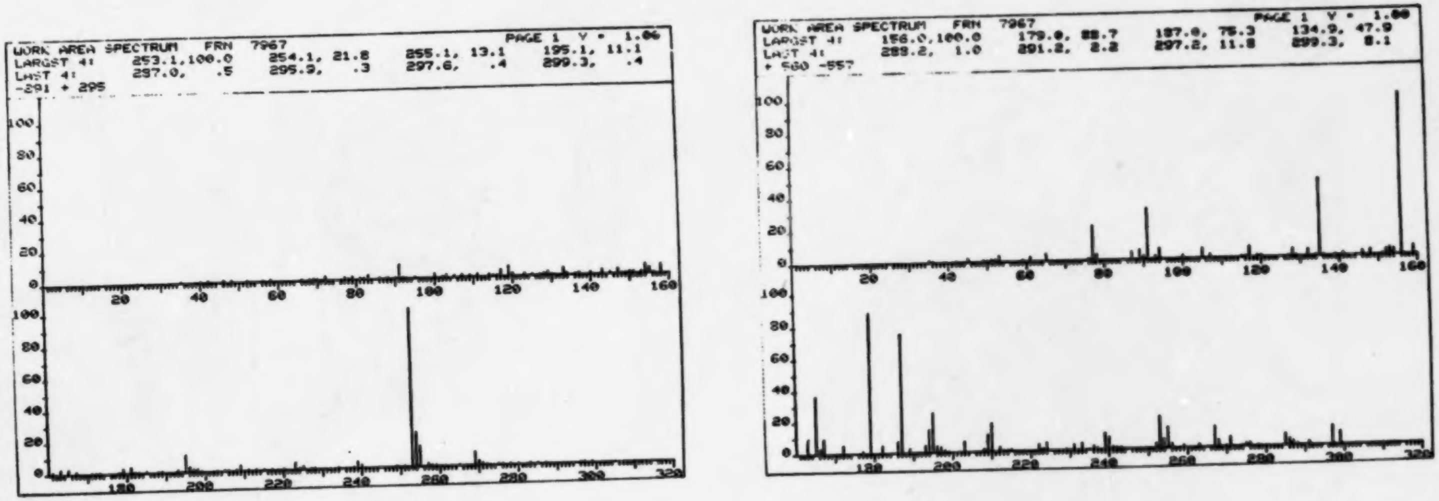


Figure 79. Total ion reconstructed chromatogram and single ion chromatograms for m/e ions 73 and 147 for water sample W-7, Union Carbide, Institute, West Virginia.

Figure 80 is the mass spectra of unknown compounds at retention times 13.9 and 25.0 min.

13.2.3 Soil and Sediment Samples

A total of eight soil samples and one sediment sample were collected at the locations shown in Figure 81 in the area surrounding Union Carbide, Institute, W.V. The samples were collected in 500 cm^3 capacity canning jars. These samples were extracted, concentrated and analyzed as described in Sections 5 and 6. None of the six β-chlorethers of interest were found in any of these nine samples. Average detections limit for soil and sediment samples for the β-chloroethers was 4×10^{-9} g/g.



(a) Unknown (RT=13.9 min)

(b) Unknown (RT=25.0 min)

Figure 80. Mass spectra of two unknowns in water sample W-7 extract (see Figure F-8 for chromatogram).

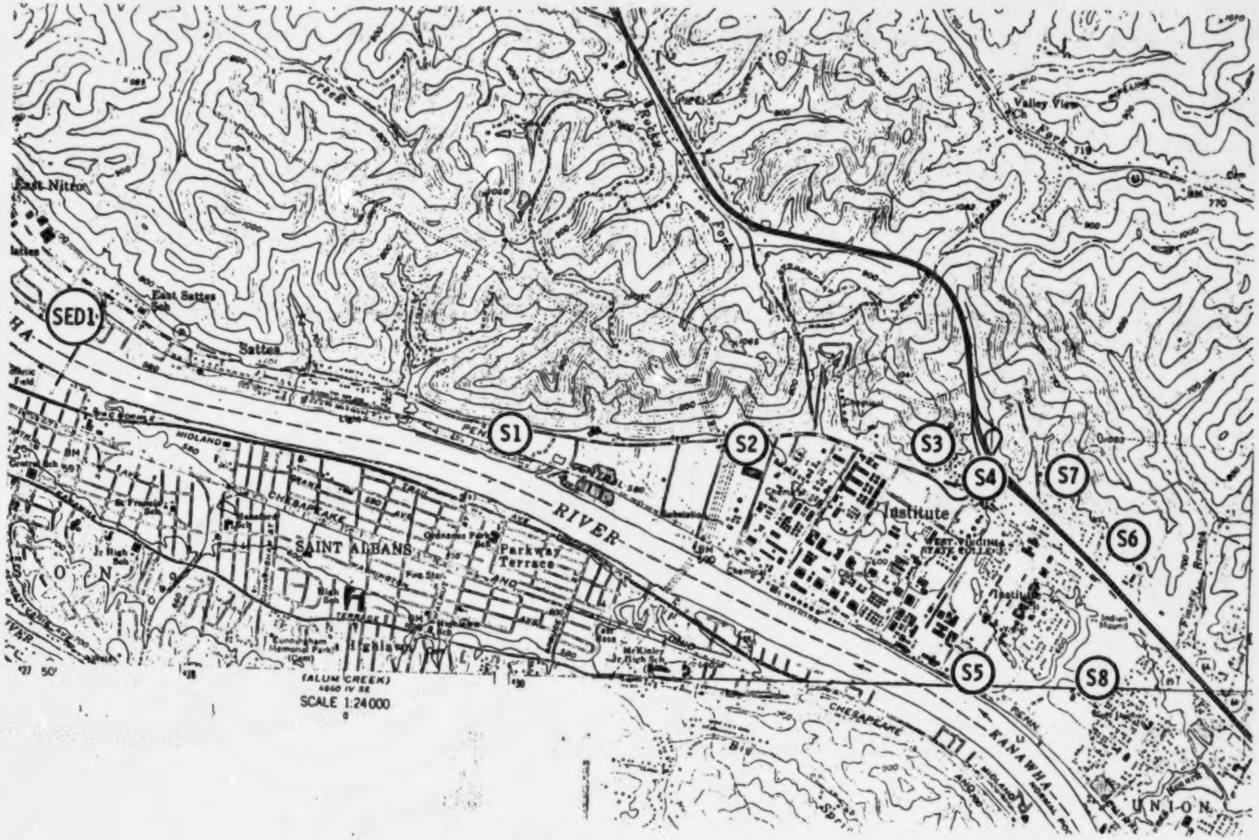

SED1
S1
S2
S3
S4
S5
S6
S7
S8
RIVER
KANAWHA
SAINT ALBANS
Parkway Terrace
Institute
East Nitro
Sattes
East Sattes
Valley View
Rocky Fork
Creek
UNION
CHESAPEAKE
MIDLAND
SCALE 1:24000

Figure 81. Soil and sediment sampling locations at Union Carbide, Institute, W. Va.

SECTION 14

SAMPLING AND ANALYSIS FOR β-CHLOROETHERS MILLIKEN CHEMICAL, INMAN, SOUTH CAROLINA

14.1 PRESAMPLING SURVEY

14.1.1 Description of the Plant Site

Milliken Chemical Division is located on Campton Road southwest of Inman, South Carolina. The plant's mailing address is P.O. Box 817, Inman, SC 29349. The plant specializes in the production of high quality, organic chemicals widely used in the textile and related industries and as intermediates in the synthesis of dyestuff and other chemical intermediates. Sampling by EPA Region IV revealed the presence of bis(2-chloroethyl) ether and 1,2-bis(2-chloroethoxy) ethane in the wastewater effluent from this plant. The plant was required in their NPDES permit issued by the South Carolina Department of Health and Environmental Control to monitor bis(2-chloroethyl) ether and 2-chloroethanol for the period 18 March 1976 through 30 June 1977.

A presurvey of the plant area was performed on 23 August 1977. The presurvey consisted of a visual inspection of the Milliken plant site, since contact with plant personnel was not allowed, and selection of sites for air and water sampling.

The Milliken Chemical Division at Inman consists of two large buildings and a number of small buildings. Only one main stack ∿ 12 m high was present at the plant site. The only visible emissions were a number of steam vents. No odor was present in the area during presurvey or sampling. The wastewater treatment and outfall of the plant were not visible from areas accessible around the plant. It was known from the NPDES permit that the water effluent of the plant was received by Lawsons Fork Creek.

The location of the Milliken plant and surrounding area known to be owned by Milliken are shown in Figure 82. The dimensions of the site are also indicated on Figure 82. The site occupies a triangular area 0.37 km x 0.3 km x 0.5 km. The short side of the triangle fronts on Campton Road. A road at one time ran through the property, but it has since been closed and fenced. The plant site is bounded on the NE by Campton Road, on the south and northwest by pine forests. Only a few houses along Campton Road near the plant. A panoramic photograph of the plant is shown in Figure 83.

14.1.2 Surrounding Area

The Inman area is located in northwest South Carolina, ∿ 8 km north northwest of the city of Spartanburg, S.C. Elevation of the area ranges from 260-290 m above sea level. The population of Inman is 1661. Two other small towns in the area are Campobello (pop. 530) and Boiling Springs (pop. 600). The population of Spartanburg is 44,546. The Milliken plant is located in Spartanburg County, S. C.

Industry in the area of the Milliken Plant included Byars Asphalt Terminal, which was 0.6 km southeast and Carolina Frozen Food, 0.3 km to the northeast. Vegetation in the area consisted of pine trees, 6 to 9 m high and 0.1 m in diameter, deciduous trees including maples and creek willows, and a number of bushy plants and vines along Lawsons Fork Creek.

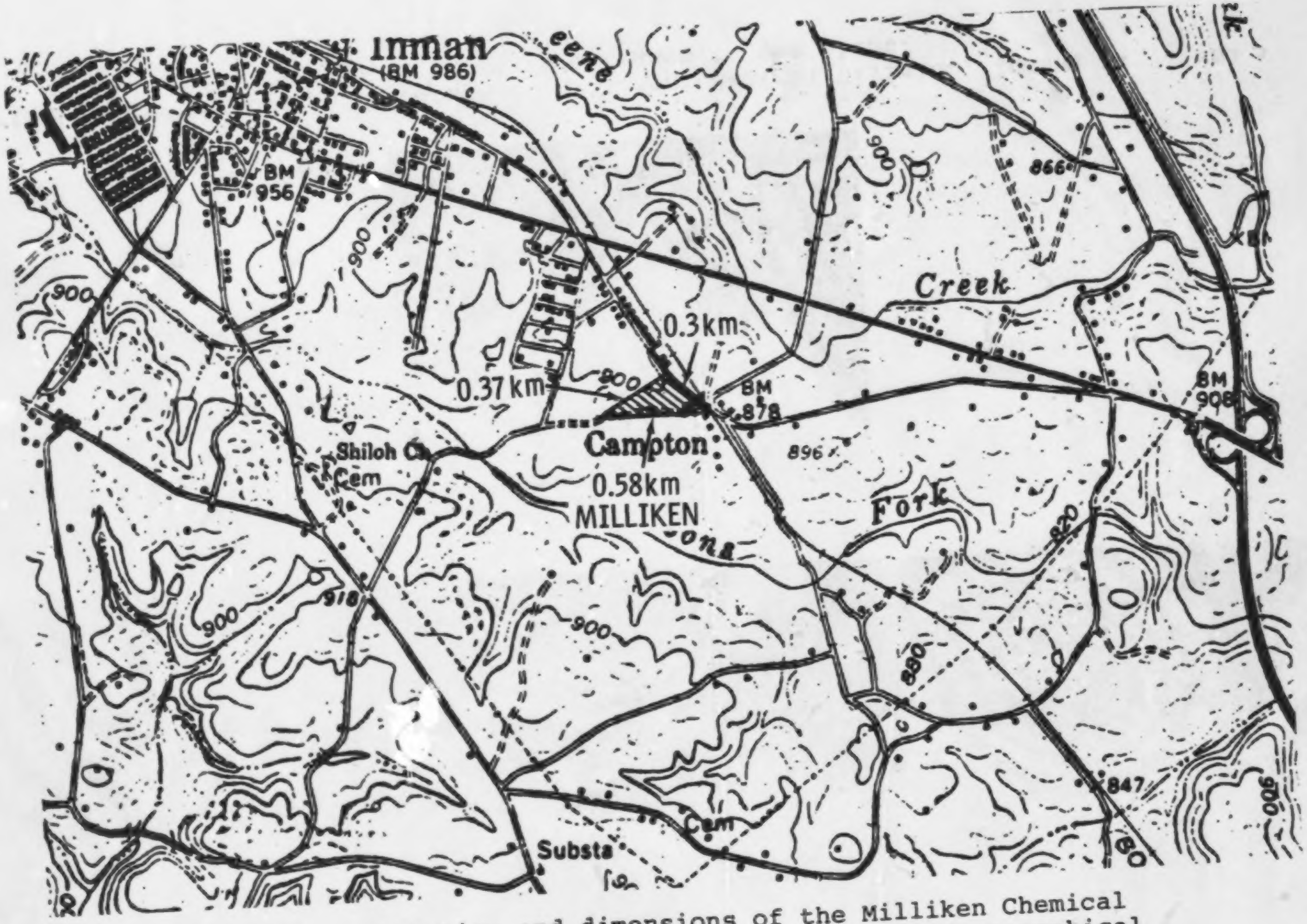

Inman
(BM 986)
BM
956
900
Creek
866
0.3km
0.37km
BM
878
BM
908
Campton
0.58km
MILLIKEN
Shiloh Ch
Cem
896
Fork
820
918
880
847
Cem
Substa

Figure 82. Location and dimensions of the Milliken Chemical Division plant, Inman, S. C. on the topographical map of the area.

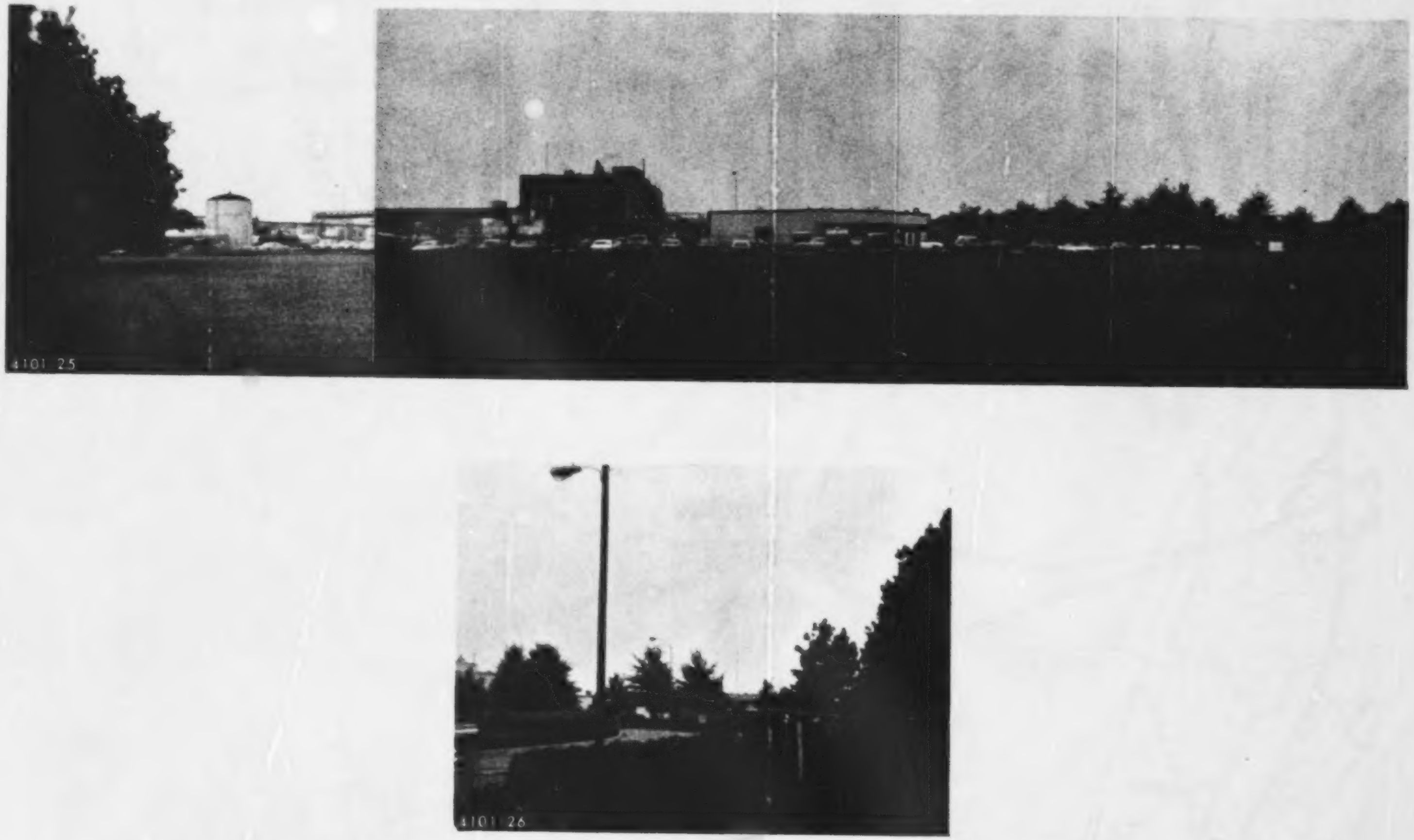

4101 25
4101 26

Figure 83. Panoramic photograph of Milliken Chemical Division, Inman, S. C. and a photograph of the main entrance to the plant.

14.2 SAMPLING AND ANALYSIS RESULTS

Sampling of the area around Milliken Chemical Division, Inman South Carolina for β-chloroethers was conducted on 23-24 August 1977. The conditions, locations and results for air, water, soil and sediment samples collected during this sampling are contained in the following subsections.

14.2.1 Air Samples

Air samplers were placed around the Milliken plant in the configuration shown in Figure 84. Seven personnel type samplers were employed for this sampling trip. A description of the samples, the Tenax tubes used to adsorb the β-chloroethers and the charcoal backup tubes are included in Section 4.1 of the main body of this report. Two samples were obtained the evening of 23-24 August 1977 and seven samples were collected during daylight hours on 24 August 1977. Table 49 lists the samples, where they were located, the compass reading relative to the center of the plant, sampling start, stop, duration and volume and β-chloroethers detected. Wind speed and direction, supplied by the weather bureau at Greenville-Spartanburg Airport, Greer, S.C. are listed in Table 50. The temperature during sampling ranged from 21°C to 31°C. A light rain shower occurred during air sampling on 24 August from 1130 to 1230. The winds during sampling, except during the shower, were very light and variable in direction. After sampling the tubes were capped with polyethylene slip-on caps and wrapped for shipment to Dayton.

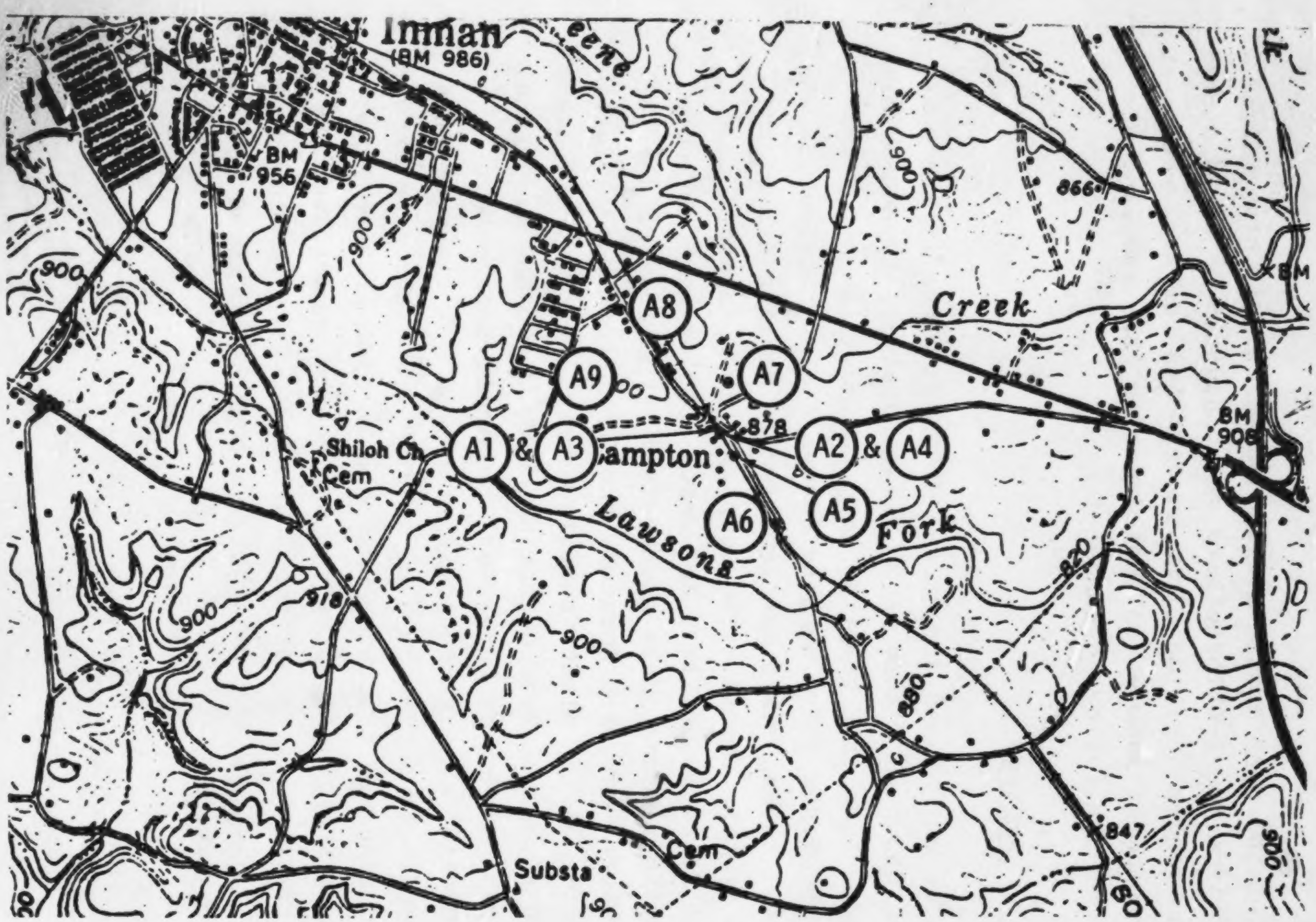

Inman
(BM 986)
BM
956
900
866
BM
Creek
A8
A9
A7
878
Shiloh Ch
Cem
A1
&
A3
ampton
A2
&
A4
BM
908
A6
A5
Lawsons
Fork
820
918
900
880
847
Cem
Substa

Figure 84. Air sampling locations at Milliken Chemical Division, Inman, S. C.

TABLE 49. AIR SAMPLING AT MILLIKEN CHEMICAL DIVISION, INMAN, S.C. 23-24 AUGUST 1977

Sample (Tenax tube)	Location	Compass reading	Sampling				β-chlorethers detected
			Time		Duration, min	Volume, liter	
			Start	End			
A-1 (G-45)	0.05 km E of Milliken, 20 m from Campton Road	60	1935 (8-23)	1010 (8-24)	875	1225	None
A-2 (G-52)	0.05 km E of Milliken, 30 m from Campton Road	80	1950 (8-23)	1027 (8-24)	877	965	None
A-3 (G-15)	0.05 km E of Milliken, 20 m from Campton Road	60	1020 (8-24)	1740 (8-24)	440	616	None
A-4 (G-40)	0.05 km E of Milliken, 30 m from Campton Road	80	1035 (8-24)	1840 (8-24)	485	485	None
A-5 (G-50)	0.10 km SE of Milliken	110	1045 (8-24)	1845 (8-24)	480	480	None
A-6 (G-51)	0.30 km SE of Milliken	140	1055 (8-24)	1852 (8-24)	477	477	None
A-7 (G-27)	0.20 km NE of Milliken	30	1110 (8-24)	1900 (8-24)	470	470	None
A-8 (G-17)	0.60 km NW of Milliken	340	1125 (8-24)	1906 (8-24)	461	461	None
A-9 (G-20)	0.60 km W of Milliken	270	1140 (8-24)	1924 (8-24)	464	464	None

TABLE 50. WEATHER CONDITIONS DURING SAMPLING AT MILLIKEN CHEMICAL, INMAN, S. C., 21-31°C

Time (Date)	Wind Speed, km/hr	 Direction, degrees
August 23, 1977		
1855	0	-
1957	7.4	150
2055	0	-
2155	0	-
2255	0	-
2355	7.4	160
August 24, 1977		
0055	7.4	170
0156	7.4	190
0257	0	-
0356	0	-
0455	0	-
0555	7.4	180
0655	9.3	170
0757	9.3	200
0857	9.3	220
0956	7.4	220
1057	25.9	140
1155	7.4	340
1255	14.8	040
1355	13.0	340
1455	7.4	270
1555	5.6	350
1655	7.4	330
1755	7.4	190
1855	0	-
1955	0	-

The tubes upon return to the laboratory were desorbed and analyzed as described in Sections 5 and 6. Air samples A-2 through A-9 were solvent desorbed and analyzed for the six β-chloroethers of interest by GC/MS/SIM. None of the samples contained β-chloroethers. Average detection limit for samples collected during daylight was 7×10^{-7} g/m^3 and 3.9×10^{-7} g/m^3 for sample A-2 collected at night. Air sample A-1 was thermally desorbed for characterization by scanned GC/MS. The total in reconstructed chromatogram for A-1 is shown in Figure 85 and the compounds identified by their mass spectra are shown on the same figure and listed below.

- 1,2-dichloroethane
- trichloroethylene
- toluene
- tetrachloroethylene
- ethylbenzene
- chlorobenzene
- benzaldehyde
- dichlorobenzene
- acetophenone
- nitrotoluene

Detection limit for the β-chloroethers for sample A-1 were $\sim 2 \times 10^{-7}$ g/m^3.

14.2.2 Water Samples

Three 24-hour composite water samples were taken during sampling at Milliken Chemical, Inman, S. C. Wastewater from the Milliken plant was known to flow into Lawsons Fork Creek, which eventually empties into the Pacolet River near Spartanburg, S.C. The locations of the one upstream and two downstream water sampling sites are shown in Figure 86.

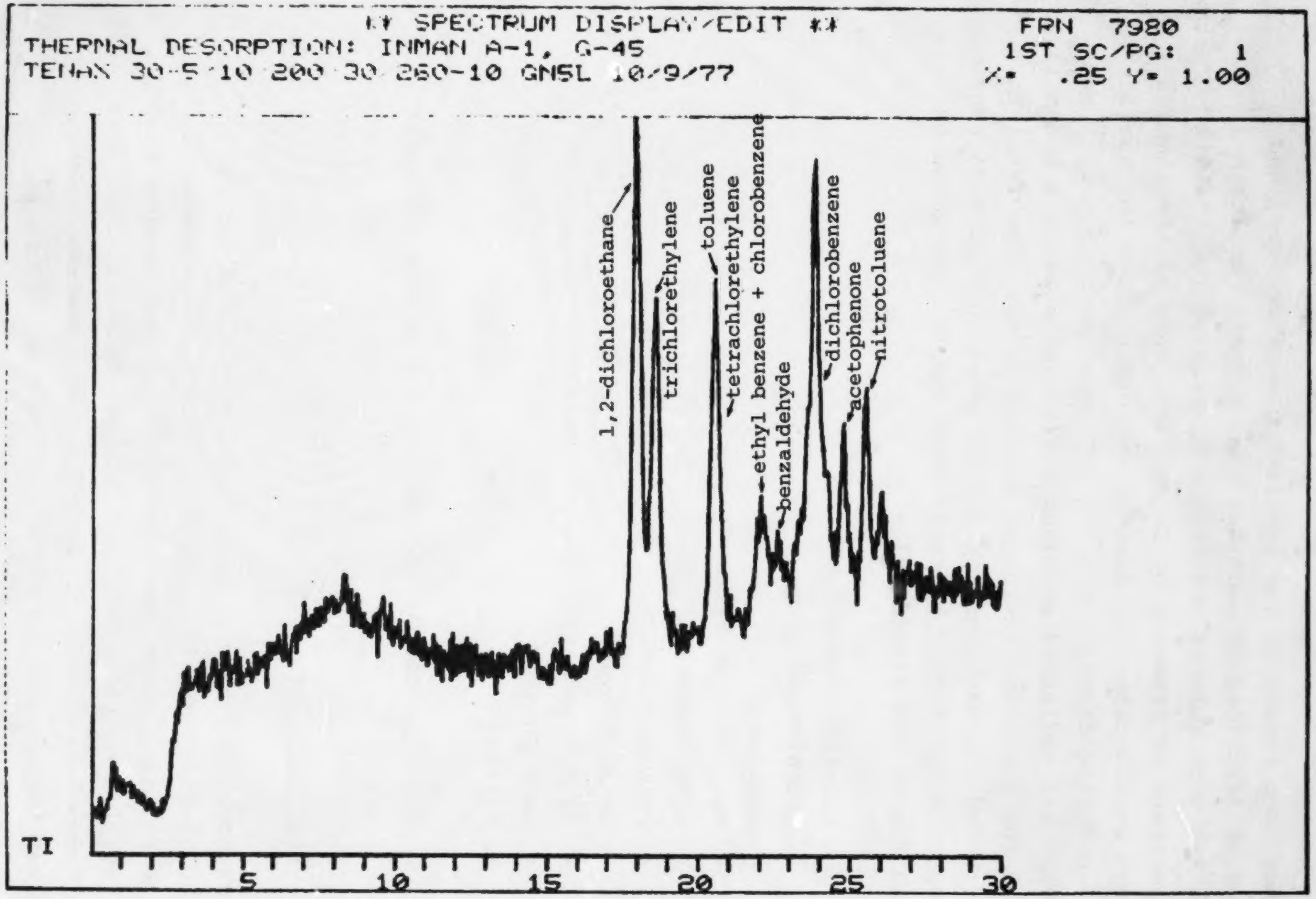


Figure 85. Total ion reconstructed chromatogram of thermally desorbed air sample, A-1, Milliken Chemical, Inman, S.C.

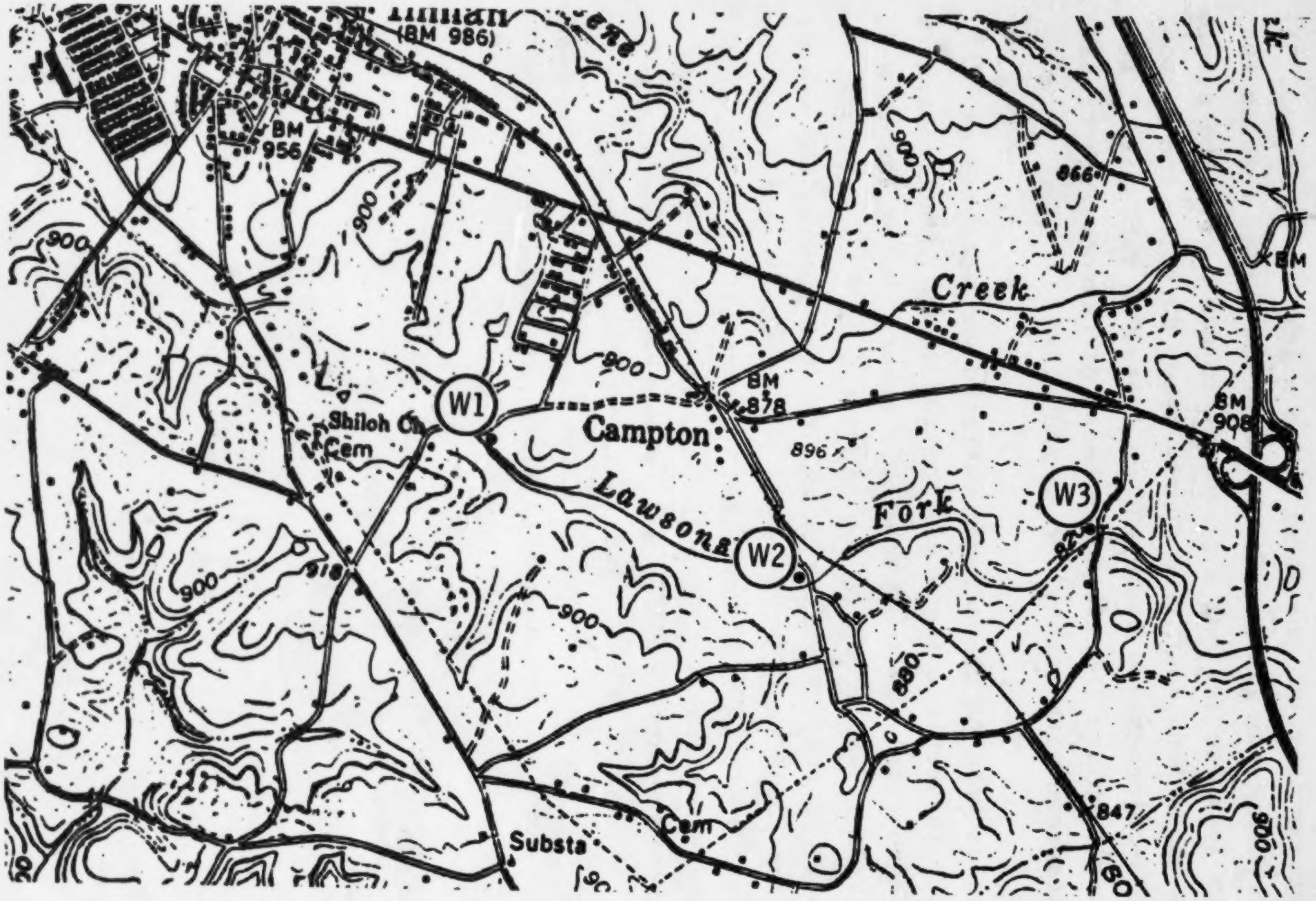

Inman
(BM 986)
BM
956
900
900
900
900
Shiloh Ch
Cem
W1
Campton
BM
878
896
Lawsons
W2
Fork
W3
Creek
866
BM
908
880
847
918
900
900
Cem
Substa
80

Figure 86. Water sampling locations at Milliken Chemical, Inman, S. C.

Lawsons Fork Creek at all three locations is ∿ 6-9 m wide. At the upstream location the water had a slight froth on top. At the two downstream locations, the water was darker than at the upstream location and had a slight petroleum odor. The sample numbers, locations, sampling start, stop, duration and volume, and the β-chloroethers detected are listed in Table 51. At all three sampling locations the banks of Lawsons Fork Creek were overgrown with bushes, trees and vines.

The samples were extracted, concentrated and analyzed as described in Sections 5 and 6. The two downstream locations were found to contain bis(2-chloroethyl) ether. Water sample W-2, downstream #1, was found to contain 4.8×10^{-6} g/l of BCEE. Figure 87 is the SIM chromatogram for W-2 showing the m/e 93 and 63 ions of BCEE. Water sample W-3, downstream #2, was found to contain 4.6×10^{-6} g/l of BCEE. Figure 88 is the SIM chromatograms for W-3 showing the m/e 93 and 63 ions of BCEE. The extract of water sample, W-2, downstream #1, was characterized further by scanned GC/MS. The total ion reconstructed chromatogram for this sample is shown in Figure 89. The peaks for which mass spectra were identified are shown in the same figure and the compounds are listed below.

- 2,6-di-tert-butyl-4-methyl phenol
- bis-(2-chloroethyl) phthalate
- unknown (RT=19.9 min)
- unknown (RT=22.1 min)
- dioctyl phthalate
- triphenyl phosphine oxide

The mass spectra of the two unknown compounds are shown in Figure 90.

TABLE 51. WATER SAMPLING AT MILLIKEN CHEMICAL DIVISION, INMAN, S.C. 23-24 AUGUST 1977

Sample	Location	Sampling				β-chloroethers detected
		Time		Duration, min	Volume, liter	
		Start	End			
W-1	Upstream, 1.2 km W of Milliken	1757 (8-23)	1755 (8-24)	1438	~4	None
W-2	Downstream #1, 1.0 km SSE of Milliken	1845 (8-23)	1815 (8-24)	1410	~4	BCEE
W-3	Downstream #2, 2.0 km SE of Milliken	1910 (8-23)	1830 (8-24)	1400	~4	BCEE

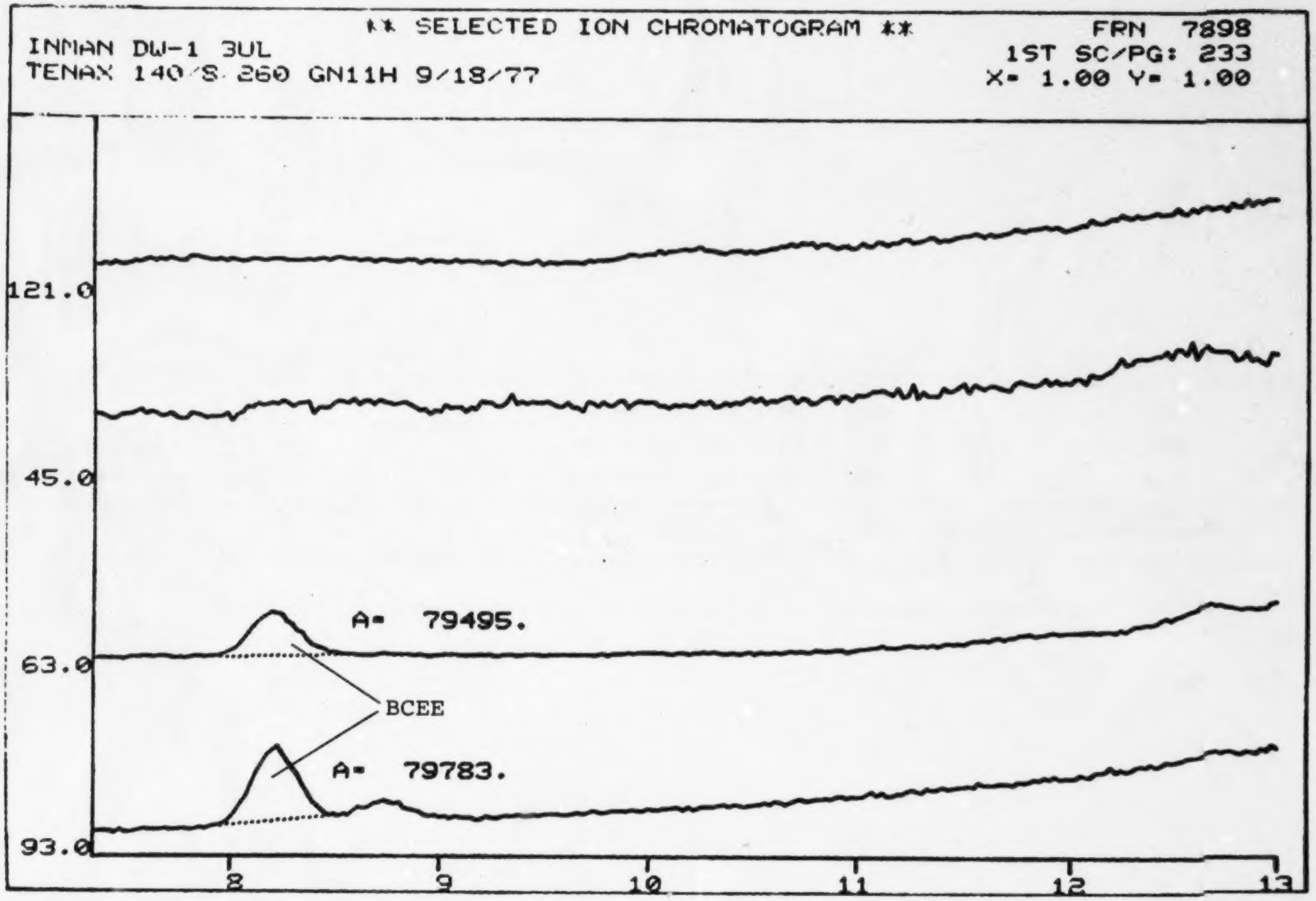


Figure 87. SIM chromatograms of water sample, W-2, Milliken Chemical, Inman, S.C.

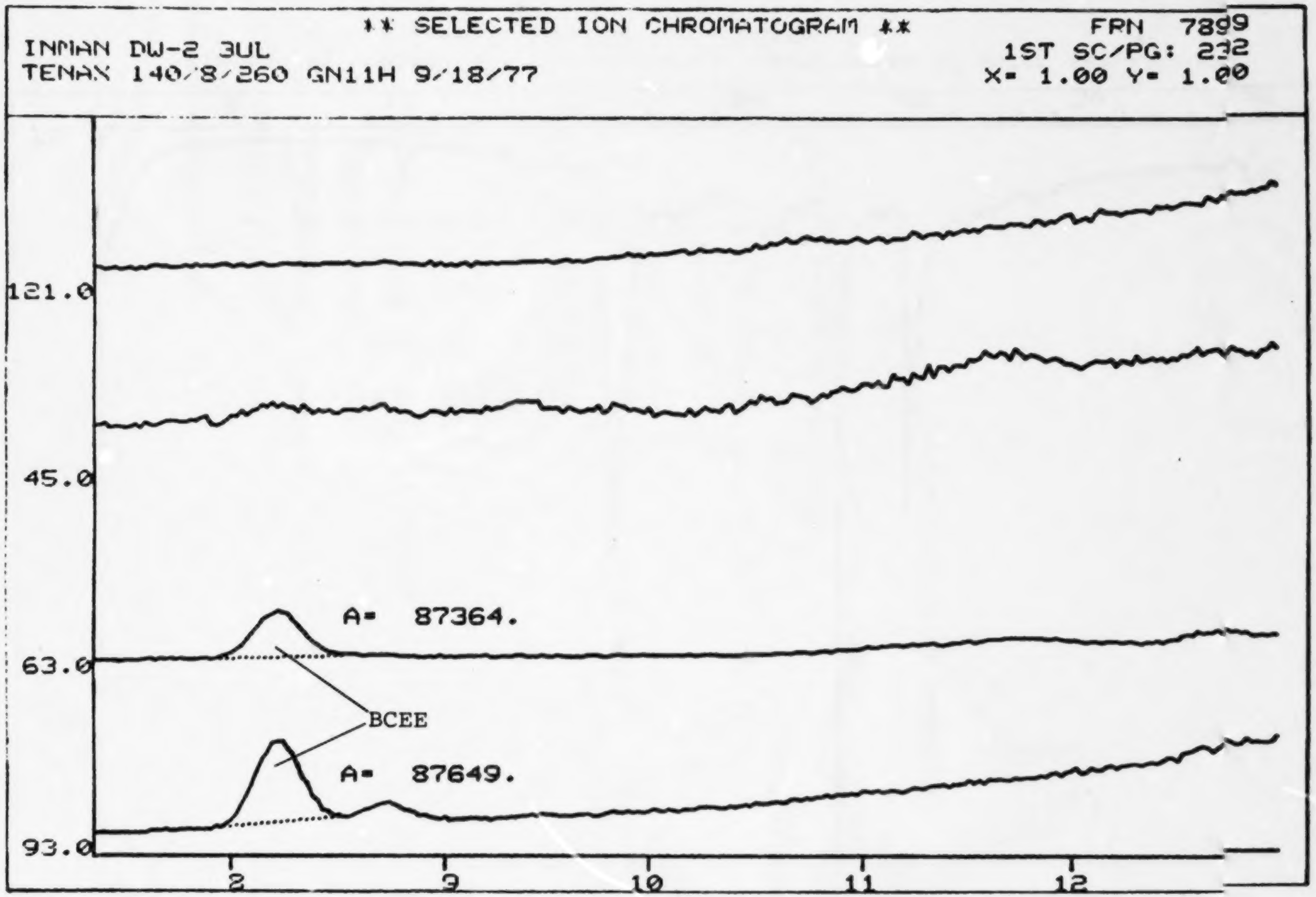


Figure 88. SIM chromatogram of water sample, W-3, Milliken Chemical, Inman, S.C.

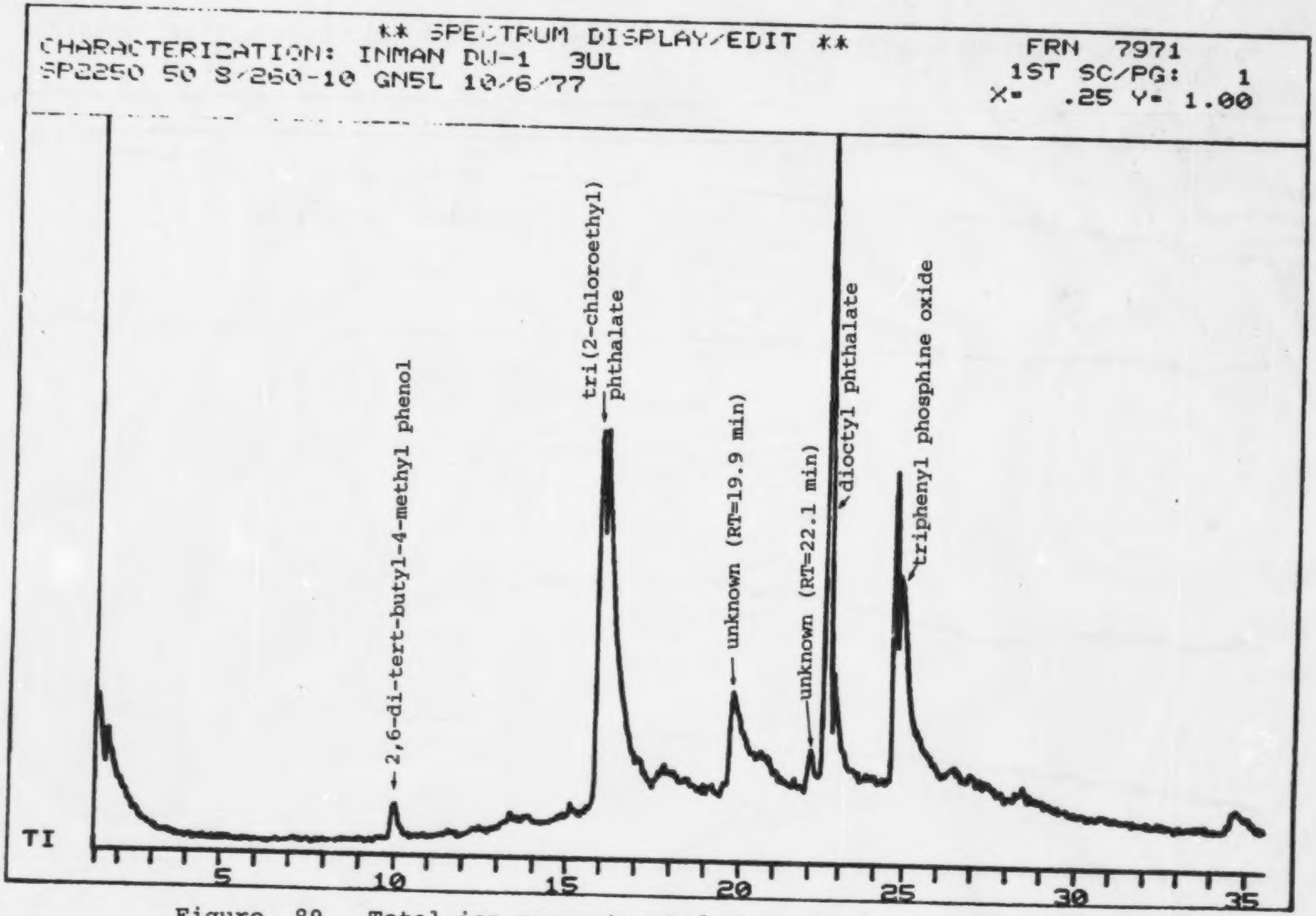
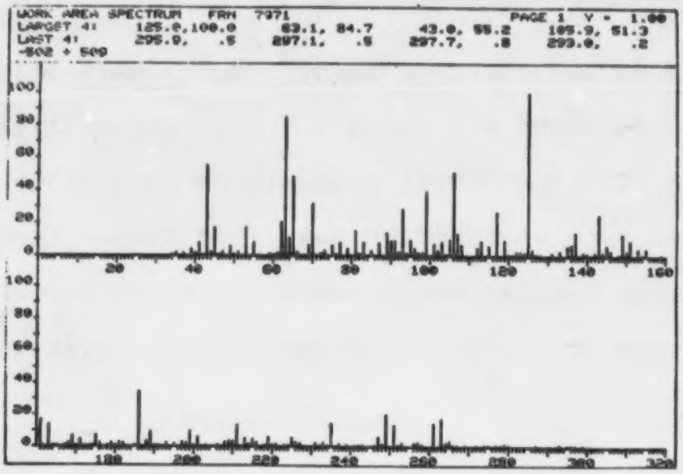
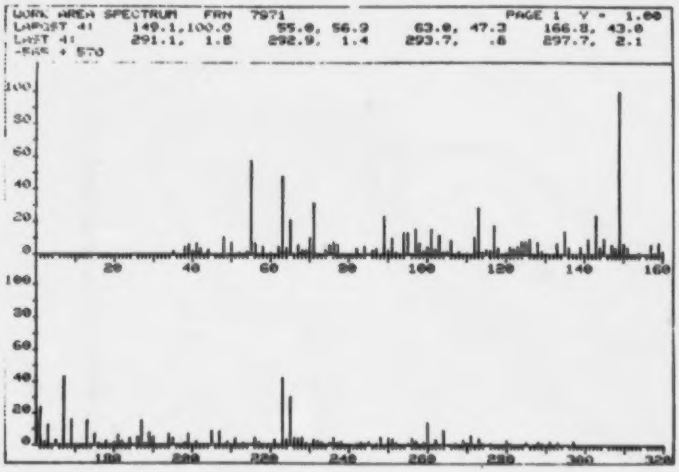


Figure 89. Total ion reconstructed chromatogram of water sample, W-2, Milliken Chemical, Inman, S.C.



(a) Unknown (RT=19.9 min)



(b) Unknown (RT=22.1 min)

Figure 90. Mass spectra of two unknown compounds, (see Figure 89).

14.2.3 Soil and Sediment Samples

Eight soil samples and three sediment samples were collected as described in Sections 4.3 and 4.4 around the Milliken Chemical plant, Inman, S. C. The sampling locations were shown in Figure 91. The samples were analyzed as described in Sections 5 and 6. None of the eleven samples contained the six β-chloroethers of interest. Average detection limit for these samples was 4×10^{-9} g/g.

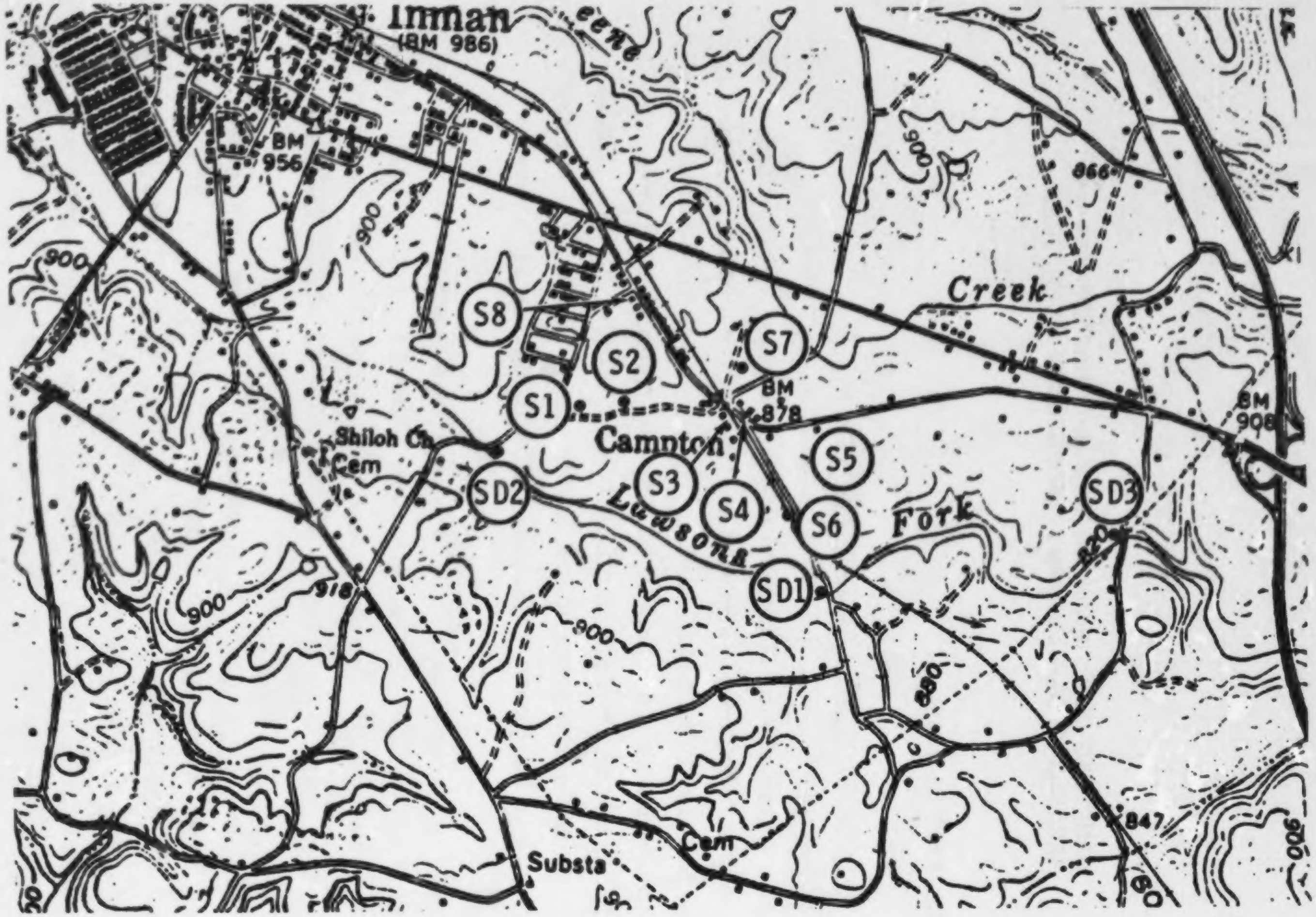

Inman
(BM 986)
BM
956
900
900
900
866
Creek
S8
S2
S7
S1
BM
878
BM
908
Shiloh Ch
Cem
Camnton
S5
S3
S4
SD2
Lawsons
S6
Fork
SD3
SD1
918
900
900
880
847
Cem
Substa
900

Figure 91. Soil and sediment samples locations around Milliken Chemical, Inman, S. C.

SECTION 15

SAMPLING AND ANALYSIS FOR β-CHLOROETHERS AT EASTMAN KODAK COMPANY, ROCHESTER, NEW YORK

15.1 PRESAMPLING SURVEY

15.1.1 Description of the Plant Site

Kodak Park Division of Eastman Kodak Company is located along Ridge Road in northwest Rochester, New York. The address for the location is 1669 Lake Avenue, Rochester, New York 14615. Kodak manufactures a large variety of chemicals for both industrial and photographic purposes. Among the chemicals reported to be manufactured at Kodak is propylene chlorohydrin, which has as a by-product bis(2-chloroisopropyl) ether.

A presurvey of the Kodak Park complex was performed on 29 August 1977. The presurvey consisted of visual inspection of the complex, since contact with plant personnel was not allowed, and selection of sites for air and water sampling.

The Eastman Kodak complex at Rochester is a huge facility occupying nine distinct locations. Chemical manufacture is performed at Kodak Park Division, 200 Ridge Road and Distillation Products Industries, 2255 Mt. Read Blvd. Well over 300 buildings are included in the site. Stacks and vents are too numerous to cite specifically. The location of the Kodak Park complex is shown on the topographical map of the area in

Figure 92. The water used by the complex is treated at the Kings Landing Waste Treatment Facility and flows into the Genesee River. Figure 93 shows a number of photographs of the waste treatment facility taken from Seneca Park across the Genesee River gorge. In the background of these photographs can be seen a few of the major buildings of Kodak Park. Figure 94 shows the dimension of the Kodak Park area. Kodak Park is bounded on all sides except the east by residencial housing and small businesses. On the east the site is bounded by the Genesee River.

15.1.2 Surrounding Area

The city of Rochester is located in northwest New York state along both sides of the Genesee River. Rochester is located in Monroe County, New York, 15 km from Lake Ontario. Elevation of the area ranges from 76 m at the lower level of the Genesee River to 160 m. The area is fairly flat except for the area around the Genesee River. The banks of the Genesee River gorge drop almost 50 m in a distance of less than 50 m at the downstream #1 water sampling location. Population of Rochester is 282,000. Vegetation in the area includes a number of species of deciduous trees. No visible emissions, other than those from power plants, and no odors were found at the Kodak site during presurvey or sampling.

15.2 SAMPLING AND ANALYSIS RESULTS

Sampling of the area around Eastman Kodak, Rochester, New York for β-chloroethers was conducted on 29-30 August 1977. The conditions, locations and results for air, water, soil and sediment samples collected during this sampling trip are included in the following subsections.

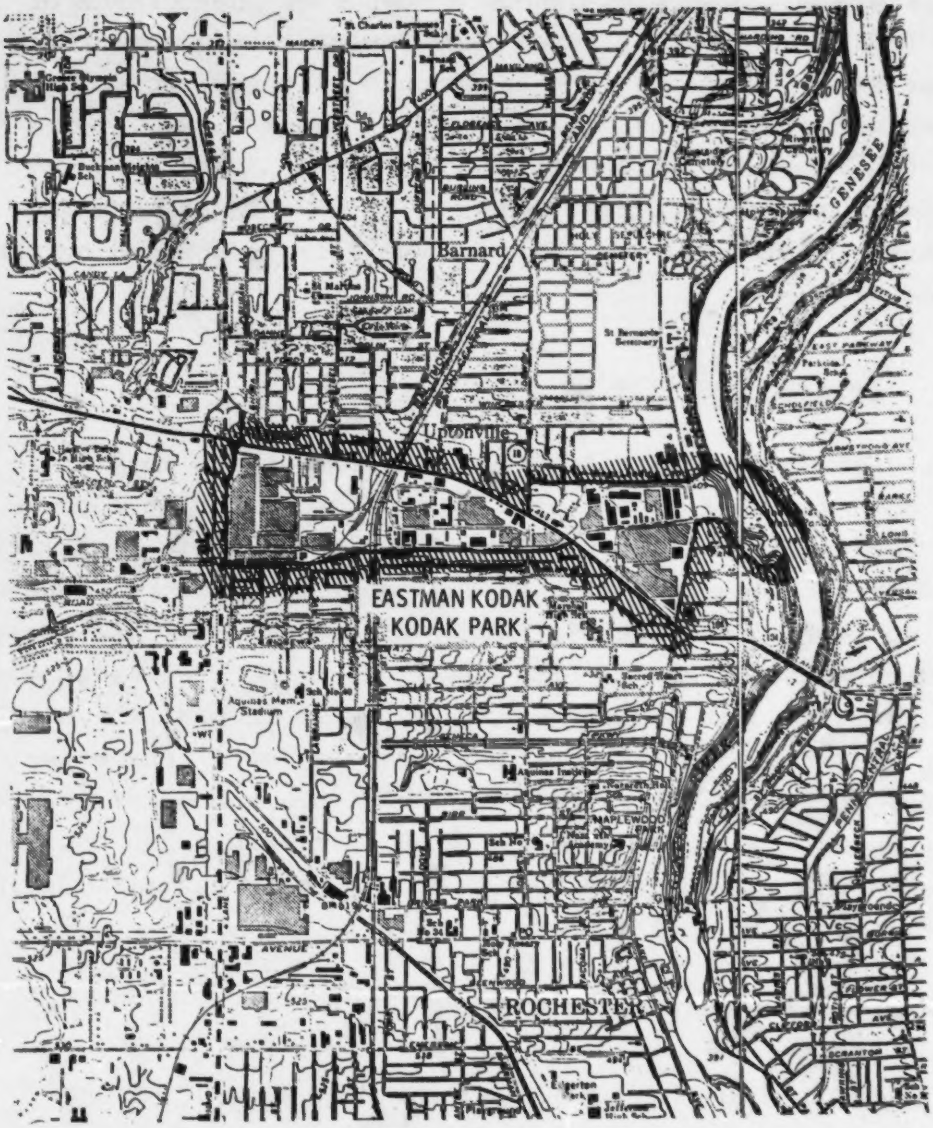
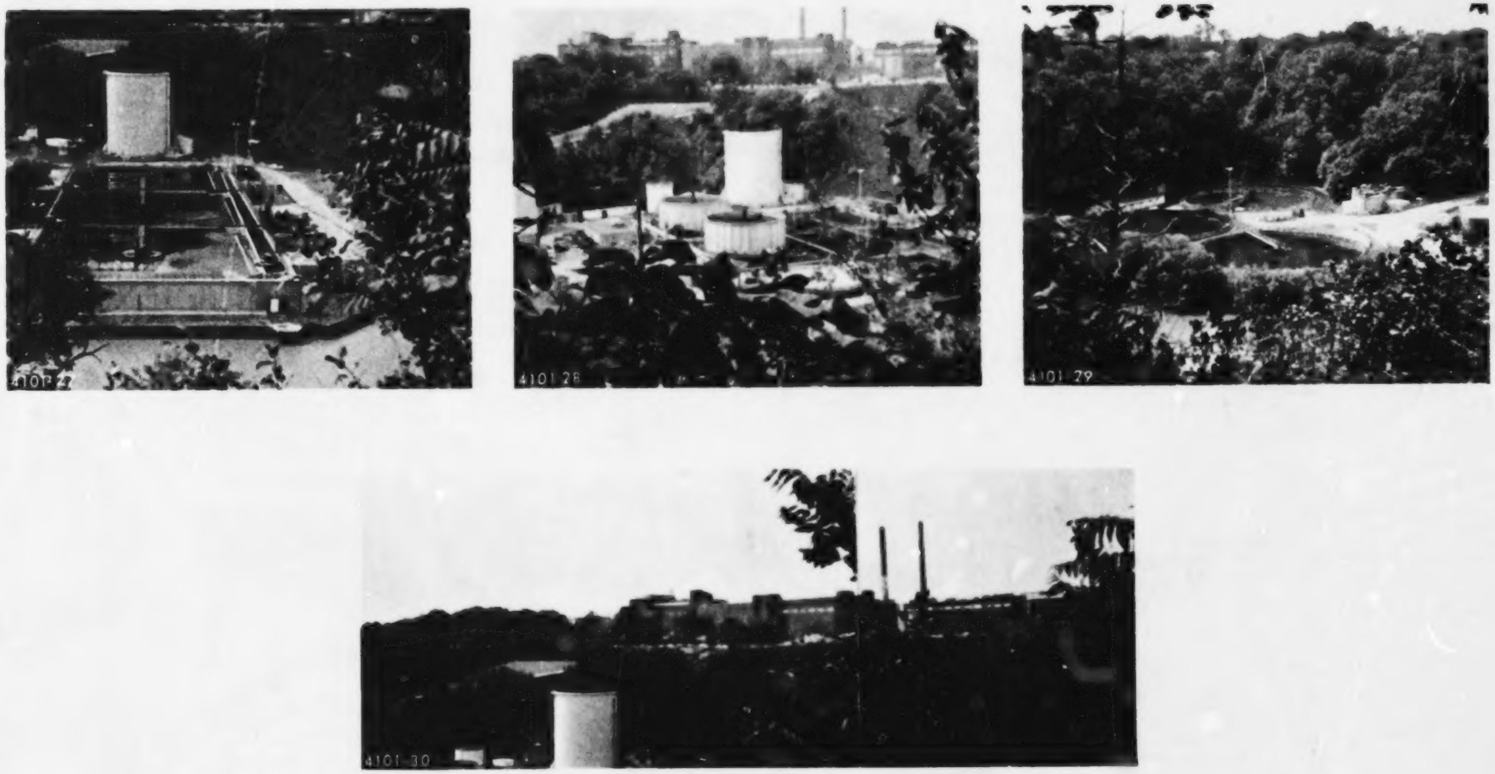

Barnard
GENESEE
Uptonville
EASTMAN KODAK
KODAK PARK
MAPLEWOOD
ROCHESTER

Figure 92. Topographical map showing Kodak Park Division, Eastman Kodak, Rochester, N. Y.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4101 28
4101 29
4101 30

Figure 93. Photographs of Kings Landing Waste Treatment Facility and portions of Kodak Park Division of Eastman Kodak, Rochester, New York.

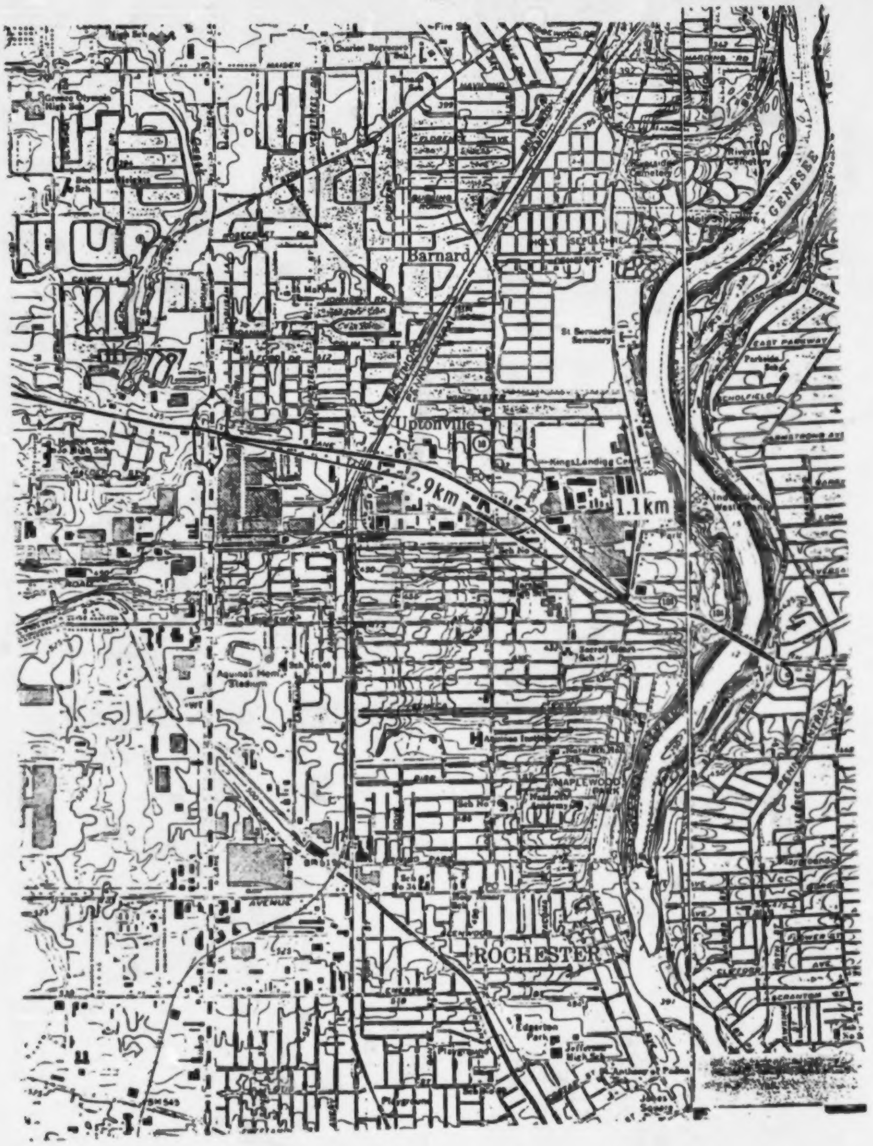

Barnard
Uptonville
2.9km
1.1km
GENESEE
ROCHESTER
MAPLEWOOD PARK

Figure 94. Dimensions of the Kodak Park Division of Eastman Kodak, Rochester, N.Y.

15.2.1 Air Samples

A total of seven air samples were collected around the Eastman Kodak complex using methods described in Section 4. The locations at which samples were collected are shown on the topographical map of the area in Figure 95. Two samples, A-1 and A-2 were collected during the night of 29-30 August 1977. Five samples were collected during the day of 30 August 1977. Table 52 describes the samples, their locations, sampling start, stop times, duration and volume, and β-chloroethers detected. Weather conditions during sampling were supplied by the weather bureau at Rochester-Monroe County Airport. The temperature ranged from 18 to 25°C. Wind speed and direction data are shown at hourly intervals in Table 53. Weather during the sampling period was very good except for light rains between 2300 on 29 August and 0100 on 30 August 1977. The sampling tubes were capped with polyethylene slip-on caps and wrapped for shipment back to Dayton.

The samples were desorbed and analyzed by GC/MS/SIM as described in Sections 5 and 6. Samples A-1, A-3 through A-7 were solvent desorbed. None of these samples contained β-chloroethers of interest. Average detection limit for A-3 through A-7 was 7×10^{-7} g/m^3 and 3.9×10^{-7} g/m^3 for air sample A-1. Sample A-2 was lost during thermal desorption analysis for characterization purposes.

15.2.2 Water Samples

Two 24-hour composite water samples were collected by the method described in Section 4 from the Genesee River downstream from the Kodak Kings Landing Waste Treatment Plant. Also, one 4-liter and two 1-liter grab samples were taken at a Rochester Light and Power Station upstream from Kodak on the

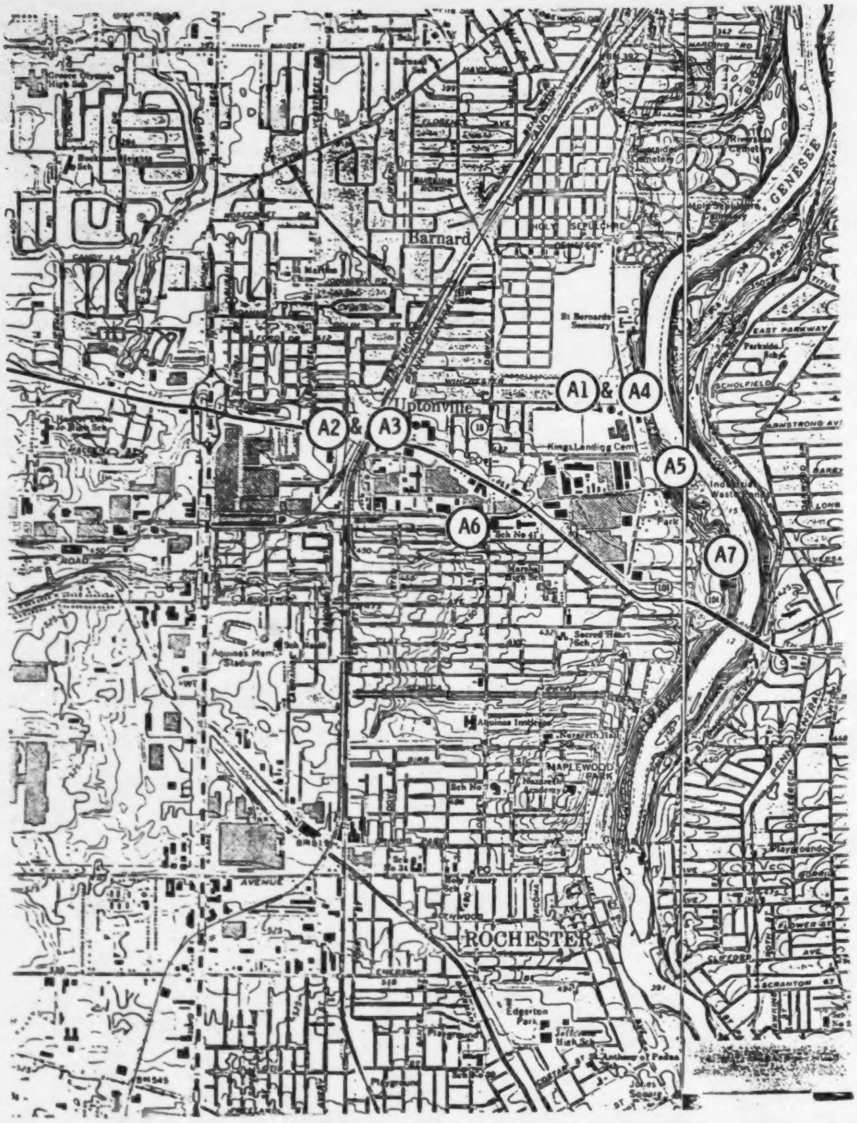

Barnard
Uptonville
A1 & A4
A2 & A3
A5
A6
A7
GENESEE
ROCHESTER
MAPLEWOOD PARK
St Bernards Seminary
Aquinas Institute
Edgerton Park
Aquinas Mem Stadium
EAST PARKWAY
SCHOLFIELD
ARMSTRONG AVE

Figure 95. Air sampling locations at Eastman Kodak, Rochester, N.Y.

TABLE 52. AIR SAMPLING AT EASTMAN KODAK, ROCHESTER, NEW YORK ON 29-30 AUGUST 1977

Sample (Tenax tube)	Location	Compass Reading	Sampling				β-chloroethers detected
			Start time	End time	Duration, min	Volume, liter	
A-1 (G-19)	10 m W of Lake Ave., 1.1 km N of NY 104	60	1615 8-29)	900 (8-30)	1005	1005	None
A-2 (G-29)	20 m N of NY 104, 0.53 km W of NY 18	330	1640 (8-39)	850 (8-30)	970	970	Lost
A- (G-32)	20 m N of NY 104, 0.53 km W of NY 18	330	900 (8-30)	1745 (8-30)	525	525	None
A-4 (G-36)	10 m W of Lake Ave., 1.1 km N of NY 104	60	920 (8-30)	1717 (8-30)	475	475	None
A-5 (G-8)	5 m from entrance to Kodak Waste Treatment Plant	100	940 (8-30)	1730 (8-30)	470	470	None
A-6 (G-38)	10 m E of NY 18, 0.23 km S of NY 104	180	1000 (8-30)	1738 (8-30)	458	458	None
A-7 (G-42)	E side of Maplewood Park Dr., 0.2 km N of NY 104	120	1015 (8-30)	1725 (8-30)	430	430	None

TABLE 53. WEATHER CONDITIONS DURING SAMPLING AT EASTMAN KODAK, ROCHESTER, N. Y., AUGUST 29-30, 1977

Date (1977) and time	Wind	
	Speed, km/hr	Direction, degrees
August 29		
1555	24.1	250
1652	20.4	250
1751	20.4	240
1850	20.4	250
1950	13.0	260
2050	5.6	140
2154	16.7	350
2251	11.1	010
2350	9.3	280
August 30		
0051	9.3	300
0150	13.0	320
0251	11.1	290
0352	11.1	290
0450	14.8	280
0550	14.8	290
0650	16.7	290
0755	14.8	260
0858	13.0	260
0953	13.0	240
1055	7.4	270
1155	13.0	320
1252	7.4	030
1355	11.1	050
1454	14.8	010
1555	14.8	020
1650	13.0	030
1753	14.8	050

Genesee River. The locations of these water sampling sites are shown on Figure 96. Table 54 lists the sampling locations, sampling start, stop, duration and volume, and β-chloroethers detected. Downstream #1 water sample, W-2, was obtained by climbing down the 50 m sides of the Genesee River behind St. Bernard's Seminary to reach the side of the river. The river at this point was ∿ 100 m wide. Downstream #2 water sample, W-1, was taken at the Old Genesee River Docks. The river at this point was ∿ 150 m wide. Photographs of the Genesee River gorge and the downstream #2 sampling location are shown in Figure 97.

The water samples were analyzed by methods described in Sections 5 and 6. None of the six β-chloroethers of interest were found in any of the water samples except the spiked sample, W-4. Results for the spiked sample are listed in Section 7.2.2. Downstream #1 water sample concentrate, W-2, was also characterized by scanned GC/MS. The total ion reconstructed chromatogram for this sample is shown in Figure 98. The identity of the peaks is shown on the figure and the compounds are listed below.

- 2,6 di-tert-butyl-4-methyl phenol
- unknown (RT=14.1 min)
- unknown (RT=15.0 min)
- butyl carbobutoxymethyl phthalate
- unknown (RT=18.0 min)
- triphenyl phosphine
- dioctyl phthalate
- triphenyl phosphine oxide

Mass spectra of the three unknown compounds are shown in Figure 99 for future reference.

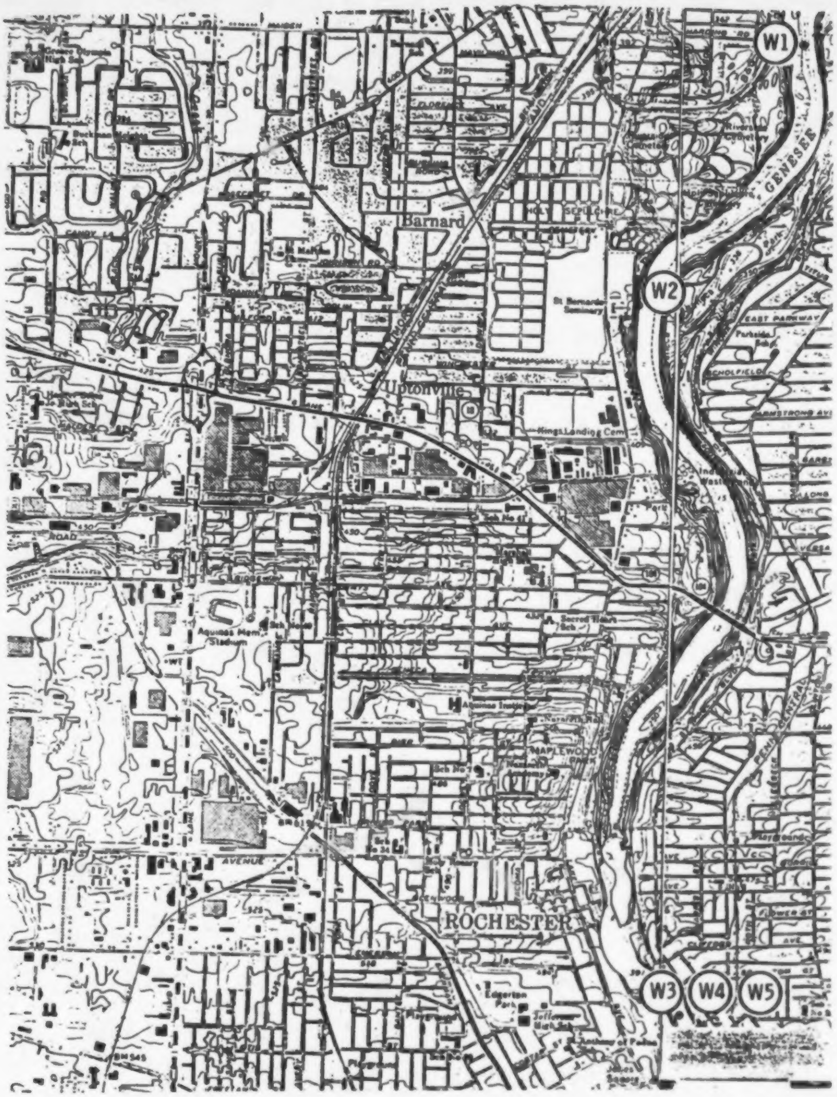

W1
W2
W3
W4
W5
GENESEE
Barnard
Uptonville
MAPLEWOOD
ROCHESTER
Aquinas Mem Stadium
EAST PARKWAY
SCHOLFIELD
ARMSTRONG AVE
AVENUE
ROAD

Figure 96. Water sampling locations at Eastman Kodak, Rochester, N.Y.

TABLE 54. WATER SAMPLING AT EASTMAN KODAK, ROCHESTER, N. Y. ON 29-30 AUGUST, 1977.

Sample (Tenax tube)		Sampling				β-chloroethers detected
		Time		Duration, min	Volume, liter	
		Start	End			
W-1	W Bank of Genesee River at Old Genesee Docks	1336 (8-29)	1615 (8-30)	1599	4	None
W-2	W bank of Genesee River behind St. Bernard's seminary	1430 (8-29)	1645 (8-30)	1575	4	None
W-3	E bank of Genesee River at Rochester Light & Power	1530 (8-29)	-	Grab	4	None
W-4	E bank of Genesee River at Rochester Light & Power - spike	1530 (8-29)	-	Grab	1	See Section 7.2.2
W-5	E bank of Genesee River at Rochester Light & Power - control	1530 (8-29)	-	Grab	1	See Section 7.2.2

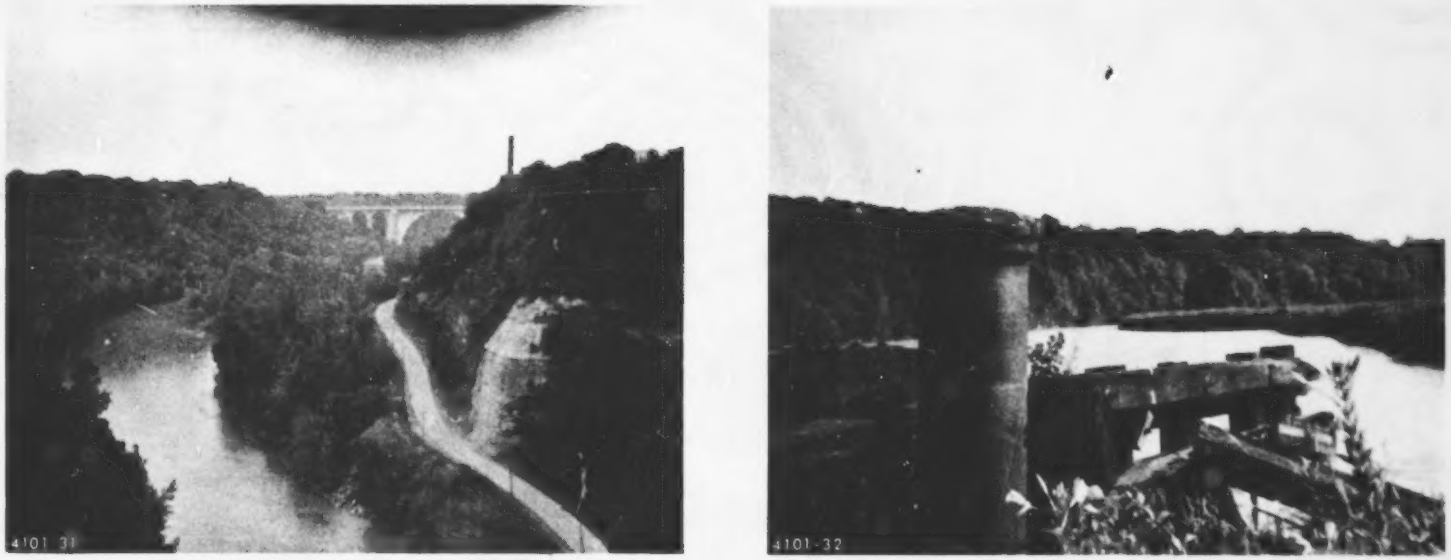

4101 31
4101-32

Figure 97. Photographs of the Genesee River gorge and downstream #2, W-1, water sampling location at Rochester, New York.

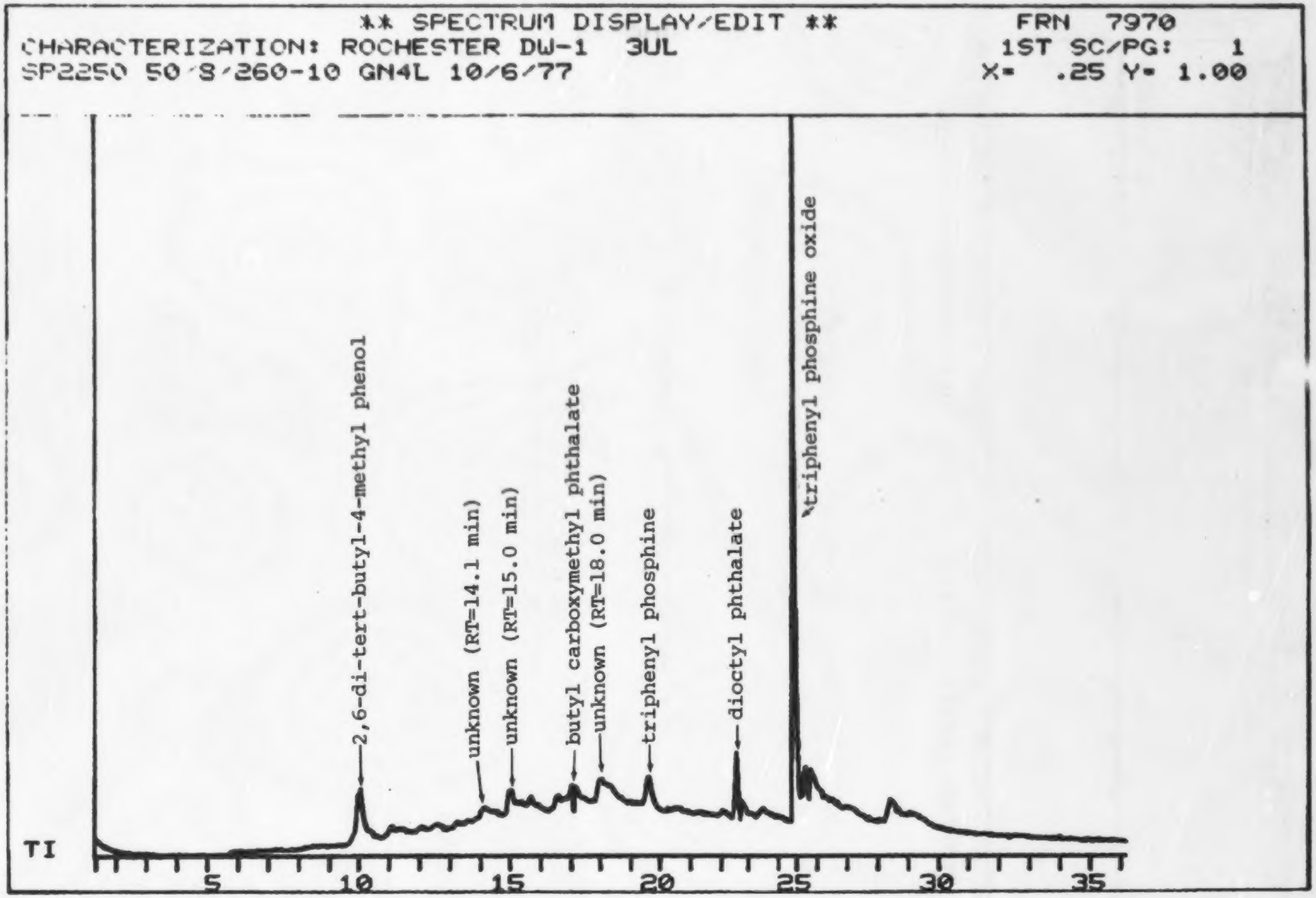
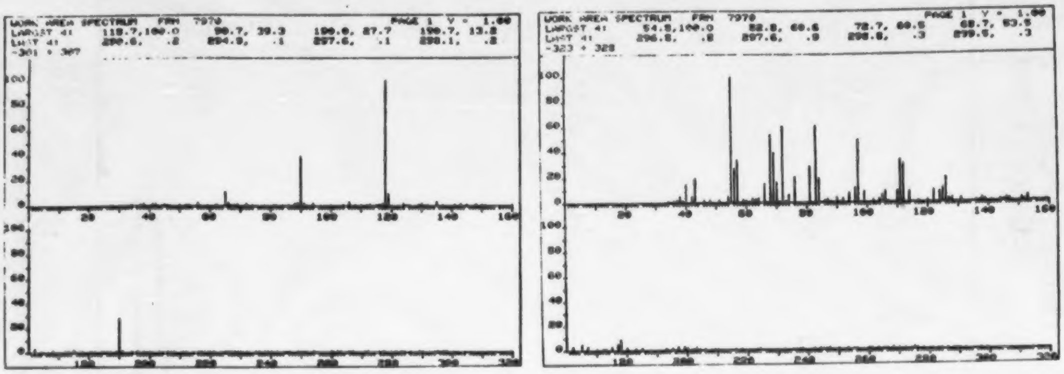
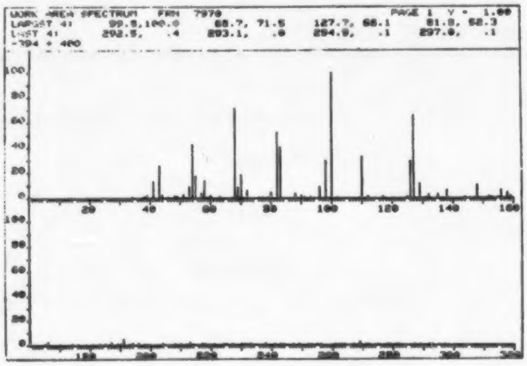


Figure 98. Total ion reconstructed chromatogram of downstream #1, W-2, water sample at Eastman Kodak, Rochester, New York.



(a) Unknown (RT=14.1 min) (b) Unknown (RT=15.0 min)



(c) Unknown (R=18.0 min)

Figure 99. Mass spectra of unknown compounds found in downstream #1, W-2, water sample (see Figure 98).

15.2.3 Soil and Sediment Samples

A total of six soil samples and one sediment sample were collected during the sampling trip to Eastman Kodak, Rochester, New York. The samples were collected as described in Section 4. Sampling locations are shown in Figure 100 on the topographical map of the area. The samples were worked up and analyzed by the methods described in Sections 5 and 6. None of the samples contained the six β-chloroethers of interest. Average detection limit was 4×10^{-9} g/g.

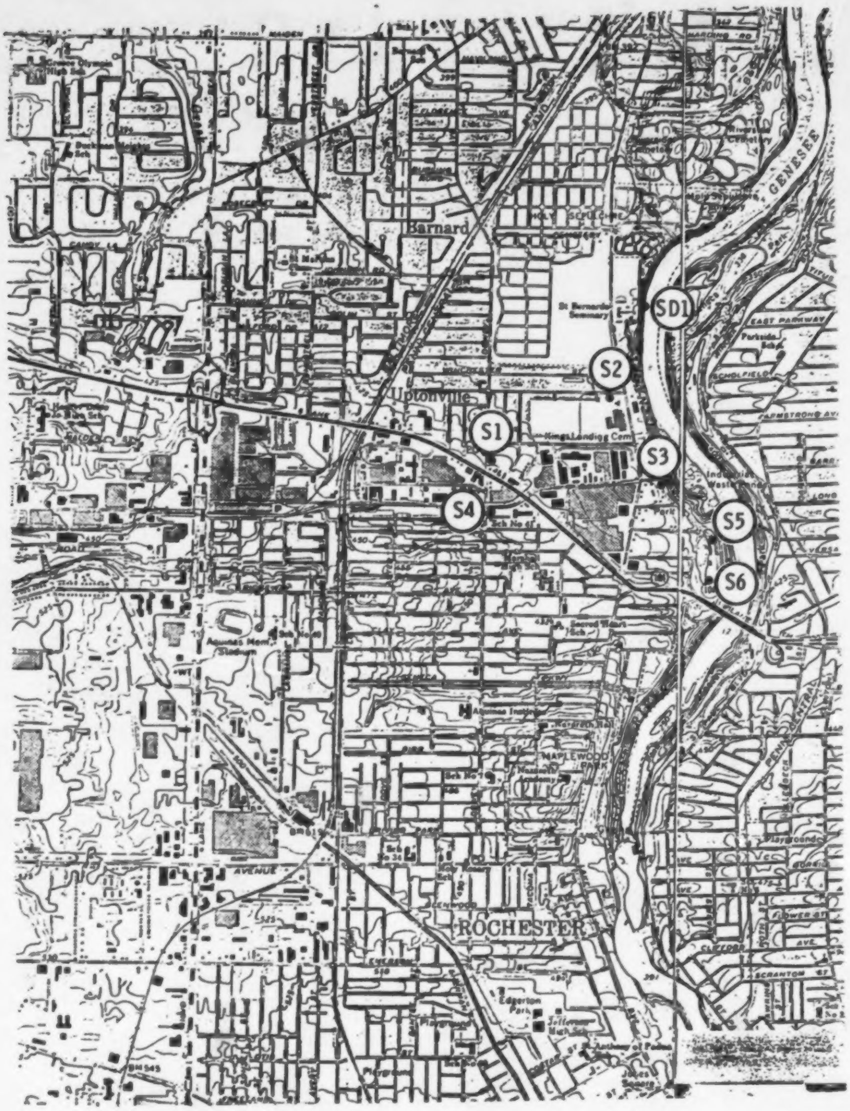

SD1
S2
S1
S3
S4
S5
S6
Barnard
Uptonville
ROCHESTER
GENESEE

Figure 100. Soil and sediment sampling locations at Eastman Kodak, Rochester, N.Y.

SECTION 16

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